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EVALUATION OF PROBLEMS RELATED TO SCALING IN
LIMESTONE WET SCRUBBING

ARTHUR D. LITTLE, INC.

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Evaluation of Problems Related to Scaling in Limestone Wet Scrubbing



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Evaluation of Problems Related to Scaling in Limestone Wet Scrubbing

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ABSTRACT

Scaling problems in limestone wet scrubbing systems have been reviewed. Thermodynamic analyses and bench scale scrubber experiments have been carried out to define the relationship between scale formation and scrubber chemistry. It has been assumed that mechanical scale deposition, due to wet-dry interfaces, stagnant areas, or poor gas-liquid distribution can be controlled through good engineering design. The approaches to controlling chemical scale deposition are: pH control, high L/G, seeding, high residence time in a hold tank, temperature control, and control of oxidation. It has been shown that sulfur dioxide removal efficiency is a linear function of pH for 0.5% CaSO_3 slurries, 0.5% CaCO_3 and 0.6% limestone slurries, and 1% CaCO_3 slurries. The calcium sulfite scrubbing system is non-scaling, but removal efficiencies are limited by the sulfite-bisulfite equilibrium to about 50%. In calcium carbonate scrubbers, sulfite scaling can be minimized while maintaining 80-90% removal efficiencies, if the pH of the scrubber effluent is controlled in the neighborhood of 5.7-5.8, where calcium sulfite is fairly soluble. An increase in temperature from 100 to 125°F seems to increase the rate of scale deposition, and in the presence of oxygen can lead to catastrophic scaling via a cementing reaction initiated by precipitation of anhydrite.

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SUMMARY

Long-term reliable operation of limestone wet scrubbers for removal of sulfur dioxide from flue gas has been limited in many cases by the deposition of calcium sulfite and sulfate scale on process equipment surfaces. The present program was undertaken to identify the fundamental factors responsible for such scaling and plugging phenomena, and to assess the possibility of controlling these factors to minimize the problem.

The literature relating to the occurrence and control of scaling in industrial processes was surveyed, and several visits were made to lime and limestone wet scrubbing installations to discuss and observe the kinds of scaling problems that are encountered in the field. In wet scrubbers, several different types of scale may be identified as follows: (1) gas inlet deposits; (2) reheater or demister deposits; (3) soft, easily removed sulfite scale; (4) hard, thin sulfate deposits on walls; and (5) catastrophically formed scale deposits which lead to rapid and complete plugging of the process equipment. In many cases, the scale appears to be mechanically deposited at wet/dry interfaces, at sharp bends in the slurry flow circuit, or in regions of poor gas/liquid distribution. Even in the absence of mechanical deposition, however, serious scaling problems have been encountered due to chemical precipitation of the reaction products, calcium sulfite and calcium sulfate, on process equipment surfaces. This program has been aimed primarily at identifying factors responsible for chemical scale deposition and developing potential control methods.

The chemical equilibria existing in scrubber slurries have been calculated for a range of typical operating conditions using computer iteration techniques. Equilibrium concentrations of the various chemical species are plotted as a function of pH and provide a useful framework for discussion of scaling and scrubber operating phenomena. Examination of the effect of pH and different chemical conditions on the concentration of chemical species active in scaling reactions yielded insights into scaling mechanisms. For example, the calculations identified a critical pH region between 5.7 and 5.9 where carbonate solid is releasing CO₂ at one atmospheric pressure; below this region no solid carbonate exists at equilibrium and the system is net dissolving with respect to calcium sulfite.

A bench-scale scrubber was designed and constructed to simulate the operation of larger sized units. Experiments were carried out with and without oxygen in the gas stream and with slurries of calcium carbonate, calcium sulfite and Shawnee (Fredonia White) limestone. The experiments were designed to explore the effects of principal operating parameters on both SO₂ absorption and scale deposition. The two phenomena are related in that the main products of the absorption reaction, calcium sulfite and calcium sulfate, are also the most troublesome scale forming solids. Furthermore, any scale control methods developed should not seriously

compromise scrubbing efficiency. The principal experimental findings with respect to SO₂ absorption may be summarized as follows. In all cases, sulfur dioxide removal efficiency increased linearly with pH over the range 4 to 7. Greater than 90% SO₂ removal was obtained with both limestone and calcium carbonate when the stoichiometry was > 1*. Removal efficiency fell off rapidly at stoichiometries < 0.7, coincident with a fall in pH below 5.7. The maximum removal efficiency with a calcium sulfite slurry alone is limited by the sulfite-bisulfite equilibrium under typical operating conditions to about 40%.

Several different types of scaling phenomena, similar to those encountered in the field, were duplicated in the bench-scale scrubber experiments. In the absence of oxygen in the flue gas, only calcium sulfite scale was formed. It built up gradually, and was manifested by an increasing pressure drop across the scrubber, and by negative and equal calcium and sulfite mass balance results. Calcium sulfite deposits formed at low L/G could be partially removed at higher L/G levels. The rate of sulfite deposition was found to be considerably more rapid at 125°F than at 100°F. Sulfite scale also formed a thin, brittle and adherent film on the wetted glass wall surfaces of the scrubber.

In the presence of oxygen, when sulfate species were allowed to accumulate, a catastrophic scaling reaction was observed, which caused sudden plugging of the flow lines. The precipitated material contained calcium sulfate, sulfite and carbonate, suggesting a cementing action initiated by the presence of sulfate.

On the combined basis of the literature review, thermodynamic analyses, and supplemental experimental work, we have identified several factors which seem to have a significant influence on chemical scale formation. These are pH, which should be as low as possible in the scrubber compatible with adequate removal efficiency (probably in the range of 5.7 - 5.9); L/G, which should be as high as possible; temperature, which should probably be less than 100°F, the transition point between gypsum and anhydrite; and oxidation, which appears to be implicated in catastrophic scale formation. The exact nature of the relationship between oxidation and scale formation has not been determined and requires further study.

Avenues of scale control that might be explored in addition, include the use of polyphosphates and polyacrylates, which have been found to be very effective in the ppm range for control of scale in many industrial processes. There is also evidence from many sources that addition of calcium sulfite and/or gypsum seed crystals to the scrubber slurry can reduce the rate of chemical scale deposition. The most effective seed concentrations, particle size, and crystal structure for given scrubber operating conditions have yet to be determined.

*Stoichiometry. Defined as the mole ratio of calcium carbonate or limestone fed to the system to the SO₂ fed to the system

CONCLUSIONS

- Several different types of scale that have been encountered in limestone wet scrubbing installations in the field are: (1) gas inlet deposits; (2) reheater or demister deposits; (3) soft, easily removed sulfite scale; (4) hard, thin sulfate deposits on walls; and (5) catastrophically formed deposits which rapidly plug the process equipment. All but type (4) have been duplicated in bench-scale experiments performed under the present program.
- Gas inlet deposits occur due to the hot gas/liquid interface in the gas inlet section. To alleviate this problem, it has been recommended that the gas duct be bent downward, and that wetted wall entrances be provided for venturi, impingement plate and flooded-bed scrubbers. For the TCA scrubber, a large rectangular inlet nozzle, which creates a sharp interface at the point where hot gases contact scrubbing liquid, has been suggested. Installation of half-track soot blowers has also been effective in eliminating massive inlet deposits in several field scrubber units.
- Reheater or demister deposits at the gas outlet from the scrubber were never sufficiently serious in our bench-scale unit to force a shut-down of operation. In large scale TCA and hydrofilter units the problems can be quite severe and no totally satisfactory solution has emerged. When the problem is in the reheater above the demister, operating experience has been better with a widely spaced steel tube-steel fin reheater coil than with a closely spaced copper coil-copper fin unit. For the demister, fiber-glass appears to be a better material than steel, but periodic washing and mechanical removal of the solids deposited is still necessary.
- Sulfite scale, which has been formed exclusively when our bench-scale scrubber is operated in the absence of oxygen, builds up gradually and is manifested by a slow increase in pressure drop across the scrubber with time on line. The deposition is partially reversible at high L/G levels.
- The extent of sulfite scale deposition in the scrubber bed can be estimated from mass balance results on calcium and sulfite, which have been shown to be negative and equal when scaling occurs.
- Since the solubility of calcium sulfite increases strongly below pH 6, the sulfite scaling problem can be minimized by operating the scrubber at as low a pH as possible consistent with adequate SO₂ removal. In our bench-scale experiments, removal efficiency

was greater than 80% down to pH 5.7 at the scrubber outlet, but dropped rapidly at lower pH levels. For other scrubbers the operating parameters should be established empirically to correspond to the optimum pH.

- Catastrophic scaling was observed in the laboratory only in the presence of oxygen, and therefore is believed to be associated with the conversion of sulfite to sulfate by oxygen in the flue gas. However, the deposit that actually plugged the lines was shown to contain relatively little calcium sulfate. Catastrophic scaling may be thus initiated by deposition of anhydrite, the stable form of calcium sulfate above 100°F, or the metastable hemihydrate (plaster of paris). Such deposits can "set" and harden under water forming a cement-like material which could result in sudden catastrophic plugging of the flow system.
- An increase in scrubber liquor temperature from 100°F to 125°F results in both an increase in the rate of deposition of calcium sulfite scale, and a decrease in the number of hours on line prior to catastrophic scaling when the flue gas contains oxygen.

RECOMMENDATIONS

- A number of additives, primarily polyphosphates and polyacrylates, have been developed and found to be effective, in the ppm range, for control of scale in many industrial processes. The feasibility of using such additives to control scale in limestone wet scrubbers should be explored.
- Although oxidation of sulfite to sulfate is implicated in catastrophic scaling, there are serious gaps in the literature on the mechanism and control of oxidation in the optimum pH and temperature range for limestone wet scrubber operation. An investigation should be carried out to evaluate means for inhibiting and promoting oxidation and to determine the effect of such treatment on scale formation.
- Seeding is a well recognized scale control technique but a systematic investigation should be carried out on optimum seed concentrations and crystal structures for maximum effectiveness.
- A dynamic mathematical model of the anticipated limestone scrubbing system should be developed to account for all steps between sulfur dioxide absorption and sulfite or sulfate precipitation. Operating conditions which minimize potential for precipitation in the scrubber should be identified by means of the model and tested experimentally.

CHAPTER I

INTRODUCTION

Purpose and Scope

The objectives of the program were to develop a basic understanding of the factors responsible for scaling in limestone wet scrubbing processes and from such understanding to devise means for alleviating the problems. To meet the objective, the following four tasks were undertaken.

Task I - Information Survey - A literature survey was prepared covering both scaling experience in alkaline wet scrubbers, and scale deposition and prevention in other industrial processes.

Task II - Thermodynamics - Equilibrium data and existing programs for calculating the distribution of components among ionic and neutral species in solution, as well as solid phases were critically reviewed. Several simple computer programs were written, based on the phase rule, for calculating activities and compositions of all species in solution in equilibrium with given typical scale forming solid phases, as a function of pH. These programs were designed to provide equilibrium data in a form most readily comparable with the experimental data obtained under Task III.

Task III - Bench-Scale Scrubber Experiments - A bench-scale scrubber was designed and built to provide a reasonable simulation of larger units in terms of L/G, gas and liquid temperature, and gas composition. A packed-bed scrubber was selected, as representative of one of the most scale-prone systems. Experiments were carried out with a view towards isolating the basic reactions of importance to the over-all scaling problem. The effects of operating parameters - L/G, stoichiometry, and temperature - on scale formation were investigated for controlled gas and scrubber feed compositions. A synthesized flue gas containing N_2 , SO_2 , O_2 , and CO_2 , in any desired proportions was used to separate the processes of SO_2 absorption and oxidation. Scrubber feed compositions investigated included 0.2N NaOH, Na_2SO_3 - $NaHSO_3$, and water in shake-down runs; 1, and 0.5 wt % $CaCO_3$ slurry; 0.5 wt % $CaSO_3$ slurry; and 0.6% Shawnee limestone slurry.

Task IV - Structural Materials Evaluation - Coupons of Monel 400, Teflon, OFHC copper, 316 stainless, 1008 low carbon steel, and borosilicate glass were immersed at six different locations within the scrubber during operation, and limited data were obtained with respect to scale deposition and corrosion.

Background

Virtually every lime or limestone wet scrubbing installation, - laboratory, pilot plant, or full scale unit - has been plagued at some point with scaling problems. In this context "scaling" may be defined as any kind of solid phase precipitation or plugging which interferes with normal continuous process operation. While there is little basic understanding of the mechanism or mechanisms of scale deposition, several qualitatively distinguishable types of scaling problems have been encountered in practice. In some cases, physical factors are clearly responsible - solid's build-up at wet-dry interfaces, solid's settling in stagnant regions, splash, filtration effects through packing, etc. In other cases, nucleation and growth of crystalline solids onto process equipment surfaces is the inevitable result of circulating the metastable supersaturated solutions of calcium sulfite and calcium sulfate formed as a consequence of the basic scrubber chemistry. It is not always easy to distinguish chemical from physical scaling, and the latter is, in any case, probably aggravated by high degrees of supersaturation in the re-circulating scrubber liquor.

The types of scaling problems that have been reported may be summarized as follows. Gas inlet and demister or reheater deposits are quite universal, and have been encountered in virtually every wet scrubber system, at least during start-up. A soft sulfite scale, which is relatively easy to clean, has been reported by Kansas Power and Light in Lawrence and by Research-Cottrell. A hard sulfate deposit, about 1/16" thick, which forms on the scrubber walls but does not appear to grow has been observed by TVA at Colbert, and in the Bischoff and Bahco scrubbers. A catastrophic scale, which forces immediate shut-down of the apparatus, was encountered in the early ICI work and has been seen more recently by Chemico. The nature of the catastrophic scale is unclear. Our own work suggests that the oxidation of sulfite to sulfate is implicated, but the scale itself may be either calcium sulfite, calcium sulfate, or more probably a complex mixture.

The literature offers a number of control measures which can be taken to minimize scale, but these are more in the nature of general principles than practical implementation plans. The basic principles are as follows:

1. Intermittently wet and dried areas must be strictly avoided.
2. All surfaces exposed to slurry must be kept well irrigated.
3. L/G should be maintained at as high a level as possible.
4. Close regulation of pH in the scrubber is highly desirable.
5. Circulation of calcium sulfate and calcium sulfite seed crystals may be used to dissipate supersaturation in the scrubber.

6. Provision of a delay tank should further aid in desuper-saturation of the circulating scrubber liquor.

Quantitative details on tolerable pH levels, seed crystal structures and concentrations, delay times, and optimum L/G levels for various practical scrubber systems are largely lacking, as are diagnostic techniques and remedial methods for obtaining acceptable gas-slurry distributions.

The Howden ICI Process

Two of the earliest wet scrubbing systems for control of sulfur dioxide emissions from power plants were set up in Fulham and Billingham around 1935. A lime or chalk slurry was used as the scrubbing medium. At Billingham, flue gas entered the base of the scrubber and ran first through primary scrubbing elements (deep vertical plates), through a grid packing, and finally to the chimney via a demister. The recirculating slurry flowed countercurrently through a nozzle plate at the top of the scrubber, onto primary liquor distributors, down through the grid packing and primary elements, into a hold tank, and finally back to the scrubber. Additional alkali, as needed to maintain the pH of the liquor leaving the scrubber at 6.2, was introduced to the scrubbing liquor as it entered the hold tank.⁽¹⁾

Many of the features of the scrubber described evolved over a period of time in response to very severe scaling problems. In the first long-term closed-loop tests conducted at Fulham, increased resistance to gas flow was noted after 25 hours of operation, and the blockage became severe enough to force a shut-down after 72 hours. A scale 2-3 inches thick was found on portions of the scrubber surfaces. Originally, it was thought that the scale formed by mechanical entrapment of suspended particulates, which cemented together upon drying in relatively stagnant areas. However, when hard deposits of pure gypsum were found in an area of the scrubber that had only been exposed to clarified liquor, it became clear that a crystallization phenomenon or chemical scaling was involved. In order to find ways to cope with the problem, Lessing⁽²⁾ undertook a rather intensive study of crystallization from supersaturated solutions of calcium sulfate. The first essential conclusion was that a 5% addition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ crystallites to the scrubber liquor could reduce the concentration of a supersaturated solution to normal solubility in 30 seconds under conditions where the same solution would remain in a metastable state for more than 6 minutes. The rate equation derived to fit the experimental data is:

$$\frac{dc}{dt} = kp(c - c_2)^2 \quad (1)$$

where c = concentration of CaSO_4 in solution at time t

c_1 = initial concentration

c_2 = final concentration

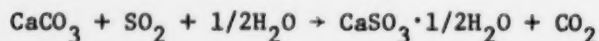
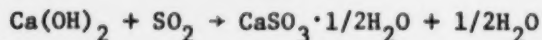
p = amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in suspension throughout the test

Equation (1) may be integrated to give the following expression:

$$\frac{c_1 - c}{c - c_2} = kpt \quad (2)$$

The value of the rate constant k depends on the shape of the suspended crystallites. Small amounts of gypsum were ineffective in promoting desupersaturation. Amounts larger than 5% offered no particular advantage from the point of view of supersaturation and added to the severity of the pumping problems.

Lessing's studies of supersaturated solutions were limited to calcium sulfate. The primary over-all scrubbing reaction, with slaked lime or limestone, involves, of course, the formation of calcium sulfite:



The presence of sulfate is believed to be due to oxidation of sulfite or bisulfite species in solution. It is not known to this day whether chemical scaling due to nucleation and growth of calcium sulfite from supersaturated solutions ever occurs. Lessing did find that the presence of calcium sulfite substantially reduces the effectiveness of gypsum as a desupersaturating agent. The rate of desupersaturation by a 5% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ slurry was halved by the presence of 4% CaSO_3 . Lessing therefore recommended the installation of an oxidizing tower after the scrubber and prior to the hold tank. At Billingham, provision was made for installation of such a tower, but it was never in fact installed. Subsequent efforts have also failed to clarify the relationship, if any, between oxidation and scaling in wet scrubber systems.

The key to eliminating scaling in the ICI wet scrubbing system was believed to lie in the understanding and control of supersaturation behavior in calcium sulfite and calcium sulfate solutions. It must be reiterated, however, that most of the fundamental work was done with the sulfate, and an analogous behavior was then assumed for the sulfite. Three steps were recommended as follows, to minimize problems due to supersaturation:

1. Limit the amount of calcium sulfite and sulfate generated in a single pass through the scrubber (the "make per pass").
2. Provide a delay tank or hold tank in the recirculation loop.
3. Circulate crystallites of calcium sulfate and sulfite, 3-5% of each in the slurry.

The reason for limiting the make per pass is to assure that the scrubbing liquor never becomes anything more than slightly supersaturated. In accord with equation (1), the lower the degree of supersaturation ($c - c_2$), the slower the rate of precipitation ($\frac{dc}{dt}$). In order to establish quantitatively the make per pass which corresponded to an acceptable level of supersaturation, a series of experiments were carried out in which sulfite and sulfate make were measured as a function of L/G and absolute liquor and gas flow rates. In one experiment, for example, conditions were changed in steps during a single run as indicated in Table I to increase the make per pass from 4-5 millieq/l to 7-8 millieq/l. At the low make level, there was no evidence of scaling, either visually or by pressure drop measurements. An increase in the make to the 5.2 - 5.7 millieq/l range produced definite evidence of some scale development. At the high make level, the increase in pressure drop due to extensive scaling eventually forced a termination of the experiment.

It should be noted that the ICI system was operated at exceedingly high values of L/G compared to those used in modern pilot plants. Even under the final operating conditions shown in Table I, where severe scaling was observed, L/G was 88. In current pilot plant practice values of L/G are typically in the 20 to 80 range, and it is seldom practical to go higher.

The delay tank is introduced into the scrubber loop to provide sufficient time to desupersaturate the scrubbing liquors before they are returned to the scrubber proper. Furthermore, the desupersaturation and resultant precipitation is forced to occur in a convenient place. The four-minute delay time built into the ICI system was found empirically to be adequate for the particular scrubber design and operating conditions specified. It is not necessarily a universally applicable figure.

Since supersaturated solutions are only metastable, at best, some desupersaturation is to be expected in the scrubber tower. When crystallites of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are circulated with the liquor, they provide preferential sites for precipitation, and hence help to prevent nucleation on solid surfaces within the scrubber. At the ICI plant in Billingham, 3-5% crystallite concentrations were maintained for both the sulfite and sulfate. In the previous work at Fulham, cited above, it was shown that sulfite crystals inhibit the desupersaturation efficiency of sulfate crystals. It is possible, however, that in conjunction with the four-minute delay time provided, the crystallite concentrations may be optimum. It is interesting to note that in one of the early pilot plant experiments at Billingham, the total suspended solids varied from 4.2% at the beginning of the run to only 9.4% at the end of 129 hours. Scaling of the grids, primarily with hard crystalline aggregates of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was very severe. Since the degree of oxidation was only 25%, the suspended gypsum in the circulating liquor stream was no more than 2%, which is woefully insufficient to discharge supersaturation in the 3-4 minute delay time permitted.

TABLE I

EFFECT OF SULFITE - SULFATE MAKE ON SCALING BEHAVIOR

	<u>First 351 Hours</u>	<u>Next 100 Hours</u>	<u>Next 200 Hours</u>	<u>Final 150 Hours</u>
Gas Flow Rate (N M ³ /hr)	5740	4100	4100	5950
Liquor Flow Rate (M ³ /hr)	100	80	70	70
L/G (gpm/1000 ft ³)	130	146	128	88
Alkali	Lime (106 hours) Limestone	Limestone	Limestone	Limestone
Make of S per mass (millieq/l)	4-5	-	5.2-5.7	7-8
Delay Time (min)	3-4	4	4	4
Sulfur in coal (%)	1.6-2	1.6-2	2	2
pH exit liquor	6	6.1	6.1	6.1
Alkali consumption (%)	100 Lime 70-80	90	90 "	120
% Suspended Solids	17-20	15	15	15
% Suspended CaSO ₄ ·2H ₂ O	4-5	5	5	5
% Suspended CaCO ₃	0.5 (Lime) 0.8 (Chalk)	0.6	0.6	1.0
% Suspended CaSO ₃	5	5	5	5
% CO ₂ in flue gas	11-13	11-13	11-13	11-13
Oxidation (%)	50	55	60	40
Scaling	None	-	Scale on wood	40

In the ICI system, limiting the make per pass, introduction of a delay tank, and circulation of calcium sulfate and sulfite crystallites helped to control supersaturation, and hence to alleviate scaling, if not to completely eliminate it under all conditions. Additional features incorporated into the scrubber design to cope with the scaling problems were:

4. Addition of fresh alkali into the circulating liquor stream just prior to the delay tank.
5. Insertion of deep, vertical plates in the lower section of the scrubbing tower.

The solubility of calcium sulfite decreases dramatically with increased pH. Hence, the addition of alkali to the scrubber effluent liquor just before it enters the delay tank helps to dissipate any sulfite supersaturation.

The vertical plates with pear-shaped tops in the bottom portion of the ICI scrubber helped to assure uniform gas distribution across the grid packing. Furthermore, scale formation on the primary elements is inhibited by the high liquor velocity and fairly high film thickness associated with them. It was found experimentally that about 50% of the sulfur was absorbed into the liquor flowing down the primary elements. This reduced the burden on the grid packing, and hence contributed substantially to safe and efficient scrubber operation.

In spite of the significant progress made by ICI in the 1930's towards prevention of scaling by proper adjustment of design parameters, occasional scaling problems were still encountered when ICI resumed scrubbing operations in the 1950's. Most of the problems were mechanical rather than chemical, however. That is, the scaling was usually due to incomplete irrigation of the scrubbing tower grids, which in turn resulted from accidental blockage of flow elsewhere in the system.

Modern Wet Scrubbing Systems

A very brief summary of operating conditions and scaling experience in a number of recently constructed wet scrubbing installations is presented in Table II. In the published literature, at least, there is a dearth of systematic studies aimed at defining a range of operating parameters for scale-free operation of the various scrubber types. Scaling has been a serious problem in most wet scrubbers, and remedial measures have been taken, with varying degrees of success, to alleviate the problems. What appears to be lacking, however, is a clear delineation of the factors responsible for scaling, and the degree to which such factors must be controlled for long-term scale-free operation. It should be recognized that, it is almost as important to know that a given set of conditions will always produce scale, as it is to know safe operating ranges for the significant parameters.

In the Howden-ICI process, scaling was alleviated to a considerable extent by (1) limiting the sulfite-sulfate make per pass to 4-5 millieq/l, (2) introducing a 3-4 minute delay time into the recirculation loop, and (3) circulating a slurry containing 3-5% of both gypsum and calcium sulfite crystallites. These values of the parameters were developed empirically for the Billingham scrubber. While the same type of control measures are probably applicable to other systems, the numerical values of the parameters are probably not optimum for different scrubber designs.

The make per mass (M_s) of total sulfur in millieq/l is related to L/G in gal/1000 ft³, the amount of sulfur in the flue gas in ppm (S_{ppm}), and the efficiency of the scrubber for SO₂ removal (ϵ) as follows:

$$M_s \text{ (millieq/l)} = \frac{0.385\epsilon (S_{ppm})}{L/G}$$

In the ICI work, the measured safe make per pass was 4-5 millieq/l. For a modern wet scrubber, operating on 2000 ppm of SO₂ in the flue gas, with typically an L/G = 50 and an efficiency of 90% ($\epsilon = 0.9$), one calculates $M_s = 11$ millieq/l, almost three times higher than the value prescribed by ICI. Delay times in the ICI scrubber, however, were 3-4 minutes. In modern practice, 10-minute delay times are more typical. It is not clear at the present time whether a trade-off is possible between delay time and make per pass. That is, it is not known whether the tolerable make per pass, or maximum acceptable supersaturation in the scrubber, is a function of the time allowed for desupersaturation in the delay tank outside of the scrubber loop.

The use of circulating sulfate and sulfite seed crystals to reduce supersaturation in the wet scrubber systems, and hence to reduce scaling, is a poorly understood phenomenon at best. For currently operating systems, very little analytical data has been recorded on percentage total solids and composition of the circulating slurry. Research-Cottrell⁽³⁾ did find that an increase in slurry concentration from 2% to the 4-8% range did help to reduce scaling. The results were in part confirmed by TVA in their 4-8 cfm scrubber⁽⁹⁾, when circulation of 1% solids led to rapid scaling, while 4% solids helped to alleviate scaling. However, delay times were also different in the two cases. Mitsubishi⁽¹⁰⁾ reports the use of seed crystals as one scale control measure, but does not present quantitative data on total solids or percentage of sulfite and sulfate in the scrubber liquor. Ontario-Hydro⁽⁵⁾ reports 12% total solids in the scrubber liquor to their spray tower - 3.6% CaSO₄·2H₂O; 6.7% CaSO₃·1/2H₂O; and 1.4% CaCO₃. Most of the scaling problems appear to have occurred at wet-dry interfaces and on poorly irrigated surfaces. On the other hand, the very high percentage of gypsum in demister deposits suggests the possibility of true chemical scaling from a supersaturated sulfate solution.

Much of the scaling experience summarized in Table II appears to be physical or mechanical, rather than chemical in nature. It is generally recognized that areas of stagnant flow, and intermittently wet and dried

areas, are to be avoided. Furthermore, experience has amply demonstrated that all surfaces exposed to the scrubber slurry should be well-irrigated.

Gas inlet deposits have been extremely common, particularly in the initial phases of scrubber operation. In most cases, these have been brought under control without undue difficulty. Combustion Engineering successfully eliminated problems of massive inlet deposits on Meramac #2 and on K, P, and L #4 by installation of half-track sootblowers on the scrubber inlet line. Prior to installation of sootblowers, the gas inlet line at Meramac became 40-50% plugged within 24 hours on line. Bechtel recommends that the gas duct be bent downward to prevent solids build-up, and further that a wet collar be provided in the duct ahead of the scrubber inlet. Wetted wall entrances, formed by use of an overflow weir that wets the inlet wall, are suggested for the venturi, impingement-plate and flooded-bed scrubbers. For the TCA scrubber a large rectangular inlet nozzle, which creates a sharp interface at the point where hot gases contact scrubbing liquid, has been proposed.

In the scrubber proper, both Research-Cottrell and Combustion Engineering have found that scale build-up can be reduced by increasing L/G. This could be due to a reduced make per pass, or simply to a mechanical flushing of surfaces where deposits might otherwise form.

In the TVA packed cross-flow scrubber⁽⁶⁾, scaling was almost certainly due to nucleation and growth from a supersaturated solution, since the deposit formed was almost pure gypsum. In contrast, in the TVA open spray tower⁽⁶⁾, mechanical deposition of a mixture of limestone, calcium sulfite, and calcium sulfate occurred in a poorly wetted region. Furthermore, the chemically deposited gypsum was hard and highly adherent, while the mechanically deposited mixture was quite soft.

In the Bischoff process⁽¹¹⁾, the formation of a pure calcium sulfite scale suggests chemical deposition. However, it is not necessarily deposition from a supersaturated solution, since precipitation of calcium sulfite is highly pH dependent. A local increase in pH could throw HSO_3^- out of solution as the solid calcium sulfite. In any case, improved flow conditions and addition of spray nozzles for intensive washing of the scrubber walls greatly alleviated the deposition problem. In general, sulfite scale is probably easier to deal with than sulfate scale, in the sense that the sulfite, even after deposition, seems to be amenable to at least partial removal by thorough flushing. Calcium sulfate tends to form a hard, tenacious scale that often has to be literally hacked out.

Scaling of demisters and reheaters on the gas outlet line has frequently been very severe. In TVA's pilot plant at Colbert, scale-free scrubber operation with 90% SO_2 removal was achieved in a simple multi-screen unit, run with a relatively high gas velocity, 16 ft/sec., and L/G = 30. However, the mist eliminators scaled severely under these conditions, inspite of the fact that they were intermittently washed

with settling tank supernatant. At K, P, and L, Lawrence, a closely spaced copper coil-copper fin reheater coil above the demister plugged regularly. Substitution of a steel tube-steel fin coil with bigger spacing alleviated the problem to a considerable extent. For the demisters, fiberglass seemed to be less prone to scaling and easier to clean by periodic washing than steel. Nonetheless, there remains some sulfate scale build-up which in practice is mechanically removed by rapping with a stick.

TABLE II

SCALING EXPERIENCE IN WET SCRUBBING FACILITIES

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichiometry %	Eff. %	Scaling Experience
Research-Cottrell (4)	Tidd	1000	Venturi & Packed Tower Packing is low ΔP , high surface area, neoprene coated asbestos Limestone slurry	30-45	4.6-6.0	10-30		• Measure scale deposition by weighing the packing. • High L/G gives less scaling than low L/G. • Hold tank residence time has no effect between 10 and 30 minutes. • Little scale at the top of the packed bed. Consistent precipitation in the bottom four elements. • Most scale was on the packing periphery; it was like mud; not hard scale. • No scale on well-irrigated surfaces. • 10.5 lbs of solid build-up in 40 hours. • 12.5 lbs of additional solid build-up in the next 40 hours.
Research-Cottrell (3) May, 1971	Tidd	1000	same; limestone slurry	45	4-8	100-120	80	• 2% slurry concentration gave much greater scaling than 4-8% slurry concentration.
Bischoff (11)	Steag	82,400	Two-stage with central spiral jet nozzles; stages separated by a sloping plate; gas enters at the top			150	85	• Incrustations and asymmetric deposits in the conical section and upper third of the cylindrical scrubber shell; analyzed almost pure CaSO_3

TABLE II (Continued)

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichiometry % Time	Eff. %	Scaling Experience
Combustion- Engineering	Union Elec.- Merri- mac	140 Mw	Furnace injection; water sprays and marble bed					- Improved by better flow and additional spray nozzles for intensive shell washing. - Rate of growth of deposits on the shell surface depended on thickness and velocity of film running down the surface.
	KPL Lawrence	125 Mw						- Sootblowers on the scrubber unit eliminated otherwise troublesome inlet deposits. - Problems of gas distribution; ladder vanes scaled. - Fiberglass is a good material to avoid corrosion. - Wash nozzles and quenching nozzles at scrubber inlets reduced deposition. - Use high L/G to prevent mechanical deposits. - Sulfite scale in drain line to clarifier; some CaO may fall into scrubber bottom, dissolve, raise pH and force as sulfite.
Combustion- Engineering	Windsor, Conn.	a) 12,000 b) 1200	a) Marble bed b) Marble bed and rod type contactors c) Bench-scale packed bed d) CFSTR-continuous flow stirred tank reaction					

TABLE II (Continued)

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichio- Time metry %	Eff. %	Scaling Experience
Detroit- Edison (12)	River Rouge	2500	1) Series of two Venturis	30- 6.0	40	100-120	60- 90	1) Series of Venturis has been run for 120 hours without plugging or scaling.
			2) Venturi followed by a sieve tray					2) The sieve tray absorber did scale due to precipitation of dissolved solids.
			3) Venturi followed by TCA					
Bechtel (13)	Mohave/ Navajo	4000	Limestone Slurry					
			1) Single stage Venturi	3.3- 7.9	100		10	
			2) TCA					
			3) Impingement tray 4) Low ΔP egg-crate packing (Heil) Lime or limestone slurry; soda ash; regeneration					
Ontario- Hydro (5)	Toronto	4000	Spray tower	12- 5.6- 12;	2-17	120-130	70- 80	• Soft, easily removed deposits in the demister and the flue gas inlet zone.
			Limestone slurry	75 6.0 3.6% gypsum 6.7% CaSO ₃ ; 1.4% CaCO ₃				• Demister deposits were 74% gypsum, 3% CaCO ₃ , and 23% ash. • Gas inlet deposit was 51% ash, 30% gypsum, 15% CaCO ₃ and 4% CaSO ₃ . • Some deposits occurred on surfaces not adequately irrigated with slurry solution.

TABLE II (Continued)

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichio- Time metry %	Eff. %	Scaling Experience
TVA ⁽⁹⁾	Muscle Shoals	4-8	Two-stage, counter current spray scrubber	40- 6.1- 100 5.2	1-5	3-7 100	97	• Tests with $\text{Ca}(\text{OH})_2$ - 1% solids and one-minute delay time gave rapid scaling; 4% solids, 10-minute delay time eliminated scaling; 3% solids, 10-minute delay time was intermediate
Union Carbide Chemico ⁽¹⁴⁾	Marrietta	1500	Two-stage Venturi (Chemico) Carbide sludge Limestone slurry	20- 60		25 90-150 130	70- 90 70	• Insignificant scale deposition in a three-day open loop test.
TVA ⁽⁶⁾	Colbert	2000	1) Venturi followed by Tellerette packed cross flow scrubber (gas $\perp$ to liquid) 2) Three-stage mobile bed (TCA) 3) Venturi followed by open spray tower	40 4.7- 6.8 10- 15 6.2		6 130-150	34- 87 90- 92 77	• Packed cross-flow scrubber operation was stopped after 125 hours due to scaling; pressure drop increased continuously during the run; scale was very hard and tenacious. Scale was 70-95% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 10-20% $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ with minor amounts of CaCO_3 and $\text{Ca}_x\text{Mg}_{1-x}(\text{CO}_3)$. • Spray tower was run for 354 hours with insignificant scaling; soft deposits of limestone and reaction products, several inches thick, formed in areas of the tower above the spray bank and not wetted by the spray.

TABLE II (Continued)

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichio- Time metry %	Eff. %	Scaling Experience
Zurn ⁽⁷⁾	Key West Paducah	1500	"Dustraxtor" - mobile unit; turbulent contact scrubber; very high effective L/G (100-500 gal/MCFM)	100-500	4.6-6.2	1-5	100	• The TCA was run for 172 hours, closed loop. The only solids build-up was a small accumulation below the bottom retaining grid of the first stage. • Scale build-up on blower blades down-stream of the scrubber. • Scale at the top of the scrubbing tube in an area of high turbulence, directly in the gas path; Analysis: 30.5% gypsum; 68% CaCO₃; 1.5% MgCO₃. • Scale also occurred on the scrubber housing at the water line.
ICI ⁽¹⁾	Billingham	3500	Vertical plate primary elements and grid packed tower in series	130-140	6	15	3.4 80-120	85-99 • See text.
Chemico Nov. 1971		1500	Two Venturi scrubbers in series					• More scaling and build-up in closed loop than in open-loop operations. • It is advisable to keep the scrubber slurry outside the path of gas flow.

TABLE II (Continued)

Company	Plant	Capacity (cfm)	Scrubber Type	L/G pH	% Solids	Delay Stoichio- Time metry %	Eff. %	Scaling Experience
Bahco (8)	Söders- jukhuset	17,700	Two-stage Venturi; lime slurry; high turbulence; rigorous cascade of droplets on gas-liquid contact	5.5- 6.0			96- 98	• 1" of scale on the scrubber walls in 7 months. Manual cleaning took 3 men 32 hours.
Mitsu- bishi (10)	Hiro- shima	1765	Plastic Grid Packed Tower Lime Slurry	50	<9		90- 98	• Free from scale at liquid flow of $70 \frac{\text{m}^3}{\text{m}^2\text{-hr}}$ and gas flow of $1.2 \times 10^4 \frac{\text{m}^3}{\text{m}^2\text{-hr}}$. • Soft deposit is usually CaCO_3 or CaSO_3 . It is controllable via pH and by avoiding stagnant positions in the scrubber. • Hard scale is due to growth of gypsum. Desupersaturation is the remedy-addition of seed crystals and use of delay tank. • Must avoid stagnant flow or positions in the scrubber dried intermittently. Gypsum often grows when liquid concentration increases in these places.

NOTES: (1) The pH values generally refer to the scrubber outlet.

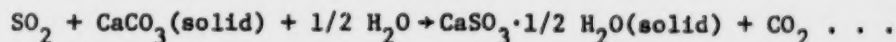
(2) The values of L/G are given in units of gal/1000 ft³, as reported by the individual companies. No attempt has been made to convert the gaseous flow rates to a common basis.

CHAPTER 2

THE CHEMISTRY OF LIMESTONE WET SCRUBBING

INTRODUCTION

The overall chemical reaction taking place in a limestone wet scrubber is quite simple:



However, the details of the equilibria established between the many gaseous, dissolved and solid species in the system and of the kinetic interactions between these species are complex. As many as six separate phases, and over twenty dissolved species may exist in scrubber slurries. Oxidation of sulfite species to sulfate species occurs simultaneously with sulfur dioxide removal from the flue gas. Additional chemical entities are continuously introduced to the system in the fly ash and in the various mineral forms of the limestone feed. The ultimate concentration level of these entities in the slurry is governed by their chemistry and the operating characteristics of the scrubber. Solid phases may exist in one of several crystal forms depending on temperature and on kinetic factors. The solubility of these solids depends on their crystal form and may be altered dramatically by supersaturation.

In order to provide a framework for the understanding of the chemistry of scrubbers, we first considered the phase rule restraints on the system, and proceeded to calculate the equilibrium concentrations of various species under likely scrubber operating conditions. We then considered the various thermodynamic and kinetic implications of these results for scaling and scrubbing reactions.

PHASE RULE CONSIDERATIONS

Determination of the equilibria existing in a scrubber slurry is much simplified by considering the restraints placed on the system by the phase rule. We will find, under the most likely operating conditions when steady state has been reached, that the equilibria can be fully specified by only two operating variables, such as pH and temperature. (In the absence of certain solid species more variables may be required.)

The phase rule defines the relationship between the following parameters:

F - the number of degrees of freedom of the system or the variables needed to completely specify it,

P - the number of phases present (gaseous, liquid and solid^{*}), and

C - the number of components which are required theoretically to synthesize the system.

Then,

$$F = C - P + 2$$

Table III summarizes the application of the phase rule for five cases of interest in wet scrubbing. Consider the simple scrubbing system (A) consisting of a calcium sulfite slurry interacting with gaseous sulfur dioxide. The number phases, P, is three - gas, liquid and solid calcium sulfite, and the number of components is also three (e.g., sulfur dioxide, water and lime). Therefore, the number of degrees of freedom is two. Temperature is conveniently taken as one of these variables. At a given temperature, the equilibria in the system are fully defined by the specification of one additional thermodynamic variable - say, pH or the equilibrium partial pressure of SO₂ above the slurry. If we now add one further component, CO₂, and a further phase, solid calcium carbonate, the number of degrees of freedom remains the same, and the system (C) is fully specified by temperature and pH.

If we now assume, for example, that some oxidation of sulfite to sulfate has occurred, but that no solid sulfate phase has yet appeared, we have added a new component (sulfate) and so must specify a further degree of freedom (e.g., sulfate concentration) to fully define the equilibria in the system (D). Once solid calcium sulfate precipitates, a new phase has been added; as one degree of freedom is removed, pH and temperature once again are sufficient to define the system (E).

A further complication is the addition of other chemical species from the fly ash and the limestone. Of particular significance are (1) magnesium compounds which will introduce a further component, magnesium carbonate, and (2) sodium and chloride which will then yield further degrees of freedom with associated variables (their concentrations) which will require specification. In this report, we do not deal with these additional materials in detail.

Several conclusions and observations may be made based on this analysis which are relevant to scaling phenomena:

* All solids are unique phases.

TABLE III

PHASE RULE CONSIDERATIONS FOR TYPICAL WET SCRUBBER SYSTEMS

<u>System</u>	<u>Solid Phases</u>	<u>Components</u> ¹	<u>Phases</u>	<u>Elected Variables</u> (C - P + 2)
A	$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$	SO_2 ; Ca(OH)_2 ; H_2O	gas, solution, one solid	T; pH
B	$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$	SO_2 ; CO_2 ; Ca(OH)_2 ; H_2O	gas, solution, one solid	T; pH; carbonate in solution
C	$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$; CaCO_3	SO_2 ; CO_2 ; Ca(OH)_2 ; H_2O	gas, solution, two solids	T; pH
D	$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$; CaCO_3	SO_2 ; CO_2 ; Ca(OH)_2 ; H_2O ; CaSO_4	gas, solution, two solids	T; pH; sulfate in solution
E	$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$; CaCO_3 ; $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	SO_2 ; CO_2 ; Ca(OH)_2 ; H_2O ; CaSO_4	gas, solution, three solids	T; pH

Notes:

1 - Other chemical components may be selected to totally specify the system, but the total number will remain the same.

1. Scales containing any proportion of calcium sulfite, calcium carbonate and calcium sulfate can be formed from typical scrubber slurries, and be at equilibrium over a range of pH and temperature. Limitations of these ranges may be set by kinetic factors and the boundary conditions imposed on other derivative variables of the system. For example, as the pH falls, the partial pressure of carbon dioxide rises and clearly can reach a limit of no more than 1 atmosphere in a practical system.
2. The amount of solid in the scrubber liquor can in no way effect the system thermodynamically; only its existence is required to establish equilibrium. Any observed change in scrubber operating parameters arising from simply increasing the slurry concentration must be due to kinetic factors, such as rate of dissolution of calcium carbonate, rate of precipitation of calcium sulfite or sulfate, or rate of solution of SO_2 .
3. A useful presentation of equilibria data can be made by displaying the concentration of equilibrium species as a function of pH at constant temperature.

CHEMICAL EQUILIBRIA IN SCRUBBER SLURRIES

With an understanding of the restraints placed on the system by the phase rule, it becomes a simpler matter to calculate the equilibrium concentrations of species in scrubber slurries. The five situations listed in Table III are considered in turn, and yield equilibrium data for all likely modes of scrubber operation.

The calculation of these equilibria, while simple in concept, is tedious to execute. Calculations must be iterated to converge the values of the activity coefficients of the dissolved species. We, therefore, have prepared a set of computer programs for use on the IBM 1100 machine to carry out these calculations.

Our approach differs from that used previously by the Radian Corporation⁽¹⁵⁾ who developed a sophisticated program which would calculate the equilibrium state achieved between given masses of input materials. This type of calculation was required in their work on the simulation of scrubber operation. Our objectives were different: namely, to generate equilibrium diagrams such that if the identify of the solids in a given slurry were known, and if certain other variables were measured, primarily temperature and pH, then all values of concentrations of ionic species and gases could be readily obtained.

The method of computation is described in detail in Appendix I. In summary, we set up the simultaneous mass law equations for the many equilibria in the scrubber, assumed starting values for the activity coefficients, and then solved the electrical neutrality equation for the calcium concentration. Next, we calculated improved activity coefficients by modified Debye-Hückel theory and repeated the process until satisfactory convergence was achieved. Convergency was tested by comparing sequential values of all significant ionic concentrations.

Sample data are presented in Tables IV, V and VI for the following conditions at 50°C (122°F):

<u>pH</u>	<u>Solids</u>	<u>Other Dissolved Species</u>
6	calcium sulfite, calcium carbonate	
6	calcium sulfite, calcium carbonate, calcium sulfate	
5.5	calcium sulfite, calcium sulfate	carbonate

These data illustrate most normal operating conditions of the scrubber and show the flexibility of the calculations.

Several observations can be made from this data. For example, the presence of sulfate has a significant effect on the equilibria at a given pH and temperature. Comparing Table V with Table IV, we see that the presence of solid sulfate suppresses the dissolved sulfite concentration which means that the solution has less capacity for absorbing sulfur dioxide. Where the rate of reaction is liquid-phase controlled (and has an L/G effect), we might expect that the pH of the solution phase would fall more rapidly on absorption of a given amount of SO₂ in the presence of calcium sulfate and thereby reduce efficiency. On the other hand, the partial pressure of SO₂ above the solution is less in the presence of sulfate, and so under conditions where the surface reaction of SO₂ is rate-limiting (no L/G effect), then we would expect the scrubbing efficiency to rise in the presence of sulfate.

Table VI illustrates a boundary condition of the system: as the pH falls, there will come a time when the pCO₂ exceeds one atmosphere, and calcium carbonate solid must completely dissolve. Under such conditions and at values of pH even lower than this, we have assumed that the most likely "quasi" equilibrium state will be the point at which pCO₂ = 1.

SPECIES	CONCENTRATION	ACTIVITY	ACTIVITY COEFFICIENT
SO3--	.4673-04	.2757-04	.5899-00
CO3--	.1007-05	.5941-06	.5899-00
HSC3-	.7372-03	.6460-03	.8764-00
HCO3-	.1009-01	.8841-02	.8764-00
H2SO3	.8007-07	.8029-07	.1003+01
H2CO3	.1710-01	.1715-01	.1003+01
CASO3	.2830-03	.2838-03	.1003+01
CACO3	.3802-05	.3812-05	.1003+01
CAHCO3+	.6703-03	.5865-03	.8751-00
CACH+	.5161-08	.4517-08	.8751-00
H+	.1122-05	.9975-06	.8893-00
OH-	.6190-07	.5417-07	.8751-00
CA++	.5125-02	.3047-02	.5946-00
TOTAL CA++	=	TOTAL SO3--	=
TOTAL SO4--	=	TOTAL CO3--	=
pSO2 =	=	pCO2 =	=
			atmospheres

Units: moles/litre

TABLE IV. EQUILIBRIUM CONCENTRATIONS AT 50°C, pH = 6 (SOLID SULFITE, CARBONATE)

SPECIES	CONCENTRATION	ACTIVITY	ACTIVITY COEFFICIENT
SO3--	.3317-04	.1451-04	.4375-00
CO3--	.7148-06	.3127-06	.4375-00
HSO3-	.4182-03	.3401-03	.8133-00
HCO3-	.5723-02	.4654-02	.8133-00
H2SO3	.4190-07	.4227-07	.1009+01
H2CO3	.8951-02	.9029-02	.1009+01
CASO3	.2814-03	.2838-03	.1009+01
CACO3	.3779-05	.3812-05	.1009+01
CAHCO3+	.7215-03	.5865-03	.8129-00
CACH+	.1055-07	.8580-08	.8129-00
H+	.1178-05	.9975-06	.8470-00
OH+	.6663-07	.5417-07	.8129-00
CA++	.1291-01	.5789-02	.4484-00
SO4--	.1017-01	.4124-02	.4056-00
HSO4-	.1042-05	.8410-06	.8129-00
CASO4	.0319-02	.6273-02	.1009+01
TOTAL CA++	= .2014-01	TOTAL SO3--	= .7328-03
TOTAL SO4--	= .1639-01	TOATL CO3--	= .1540-01
pSO2	= .7845-07	pCO2	= .4825-00
			atmospheres
		Units: moles/litre	

TABLE V. EQUILIBRIUM CONCENTRATIONS AT 50° C, pH = 6 (SOLID SULFITE, CARBONATE AND SULFATE)

SPECIES	CONCENTRATION	ACTIVITY	ACTIVITY COEFFICIENT
SO3--	.3353-04	.1477-04	.4404-00
CO3--	.1471-06	.6478-07	.4404-00
HSO3-	.1344-02	.1095-02	.8146-00
HCO3-	.3743-02	.3049-02	.8146-00
H2SO3	.4267-06	.4303-06	.1009+01
H2CO3	.1855-01	.1871-01	.1009+01
CASO3	.2814-03	.2838-03	.1009+01
CACO3	.7695-06	.7761-06	.1009+01
CAHCO3+	.4638-03	.3776-03	.8142-00
CAOH+	.3274-08	.2666-09	.8142-00
H+	.3722-05	.3155-05	.8477-00
CH-	.2103-07	.1713-07	.8142-00
CA++	.1261-01	.5688-02	.4511-00
SO4--	.1026-01	.4197-02	.4089-00
HSO4-	.3348-05	.2726-05	.8142-00
CASO4	.6220-02	.6273-02	.1009+01
TOTAL CA++	= .1958-01	TOTAL SO3--	= .1659-02
TOTAL SO4--	= .1649-01	TOTAL CO3--	= .2276-01
pSO2	= .7996-06	pCO2	= .1000+1

atmospheres

Units: moles/litre

TABLE VI. EQUILIBRIUM CONCENTRATIONS AT 50°C, pH = 5.5 (SOLID SULFITE AND SULFATE;
DISSOLVED CARBONATE, pCO2 = 1)

Table VI gives data for the situation at 50°C and pH = 5.5 where $p\text{CO}_2$ is held at a value of 1 and solid calcium carbonate is no longer present. Clearly, if this solution were allowed to equilibrate with flue gas or with air, the $p\text{CO}_2$ and the concentration of carbonate species in solution would fall still further; but under dynamic scrubber conditions, it is unlikely that there will be sufficient time for the $p\text{CO}_2$ to fall back to ambient levels.

In Figures 1 and 2 we have plotted the total solution concentrations of the major chemical components of the system - calcium, sulfite, carbonate and sulfate - as a function of pH. These plots yield several insights into scrubber operation and possible scaling mechanisms.

First, it is instructive to follow the changes in system equilibrium as sulfur dioxide is added. Referring to Figure 1, we can assume that the slurry starts at a pH of around 8. As sulfur dioxide is added to the slurry, the pH falls; the total sulfite and total carbonate concentrations rise as the proportion of bisulfite and bicarbonate in solution increases. Solid calcium carbonate dissolves, and solid calcium sulfite is precipitated. At a pH of about 5.95, the $p\text{CO}_2$ reaches 1 atmosphere, and the pH will then remain relatively constant as CO_2 is evolved, while more SO_2 is absorbed until all the solid calcium carbonate is consumed. At this point, the pH will once again continue to fall. The behavior of ionic concentrations beyond this point is complex. The calcium ion concentration goes through a minimum as the level of carbonate species fall, and rises again as more SO_2 is absorbed; the concentration of sulfite species rises to dominate the dissolved species.

The addition of sulfate to the system alters the behavior to some extent as shown in Figure 2. The pH at which solid carbonate is lost from system drops to about 5.8. The carbonate and sulfite concentrations remain about the same, but the calcium concentration is increased by about a factor of five in the pH range of normal scrubber operation. The total dissolved sulfate concentration is relatively invariant with pH, but passes through a slight maximum at a pH of about 5.7. Thus, as the pH drops toward this value, sulfate will be dissolving (so long as further oxidation is not occurring); but below this value of pH and as the pH continues to fall, sulfate is expected to be precipitating solely due to the pH change.

In the sulfate system, the calcium concentration varies much less with pH than it does in the system not containing sulfate.

In Figures 3 and 4, we show more detail of the individual ionic concentrations as a function of pH in the absence and in the presence of solid calcium sulfate. We believe that these data can be used as a basic display for discussion of scaling and scrubber performance phenomena. In most cases, the scrubber will be operating in regions where

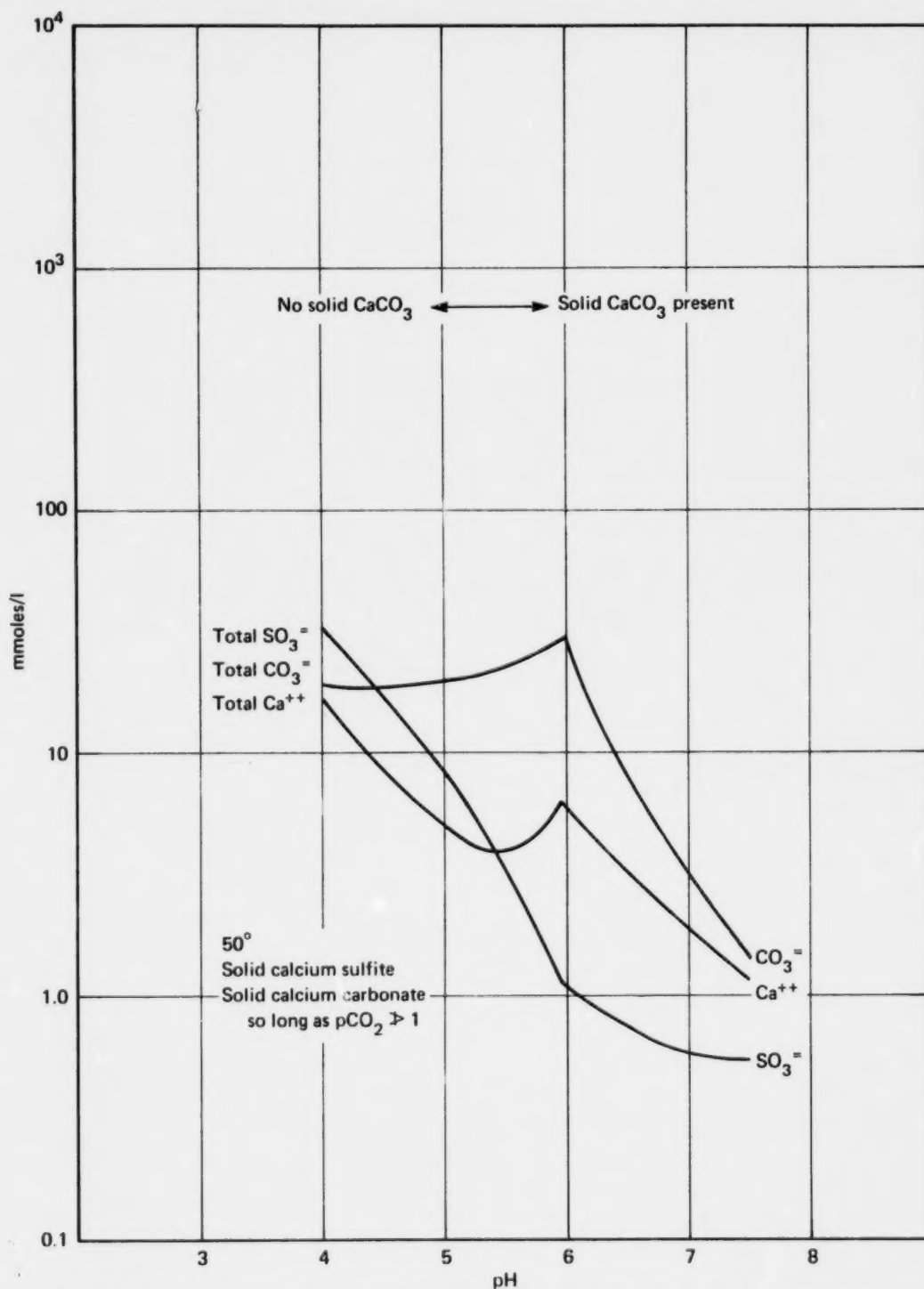


FIGURE 1. TOTAL DISSOLVED CHEMICAL SPECIES IN A SULFITE, CARBONATE SLURRY SYSTEM

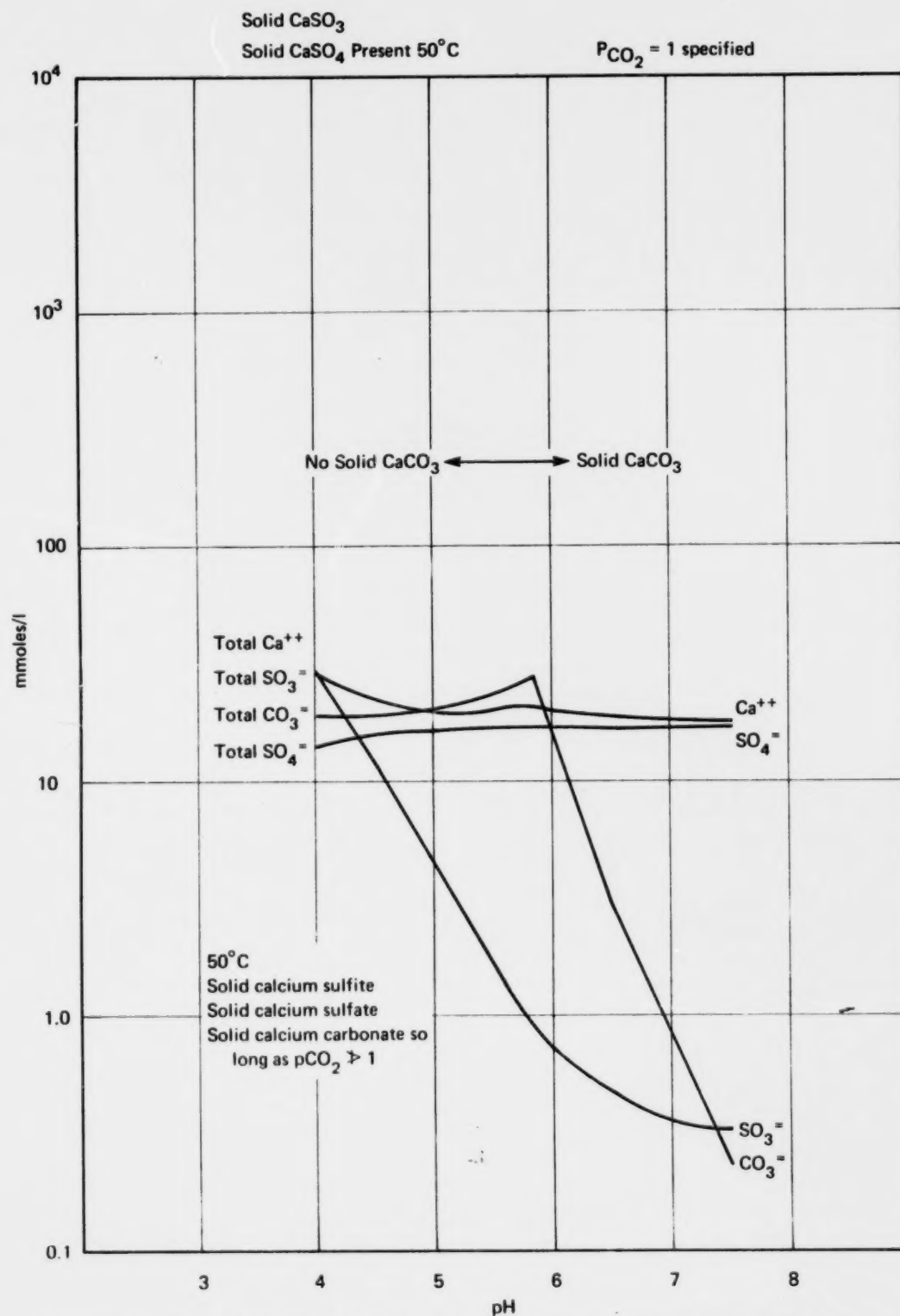


FIGURE 2. TOTAL DISSOLVED CHEMICAL SPECIES IN A SULFITE, CARBONATE, SULFATE SLURRY SYSTEM

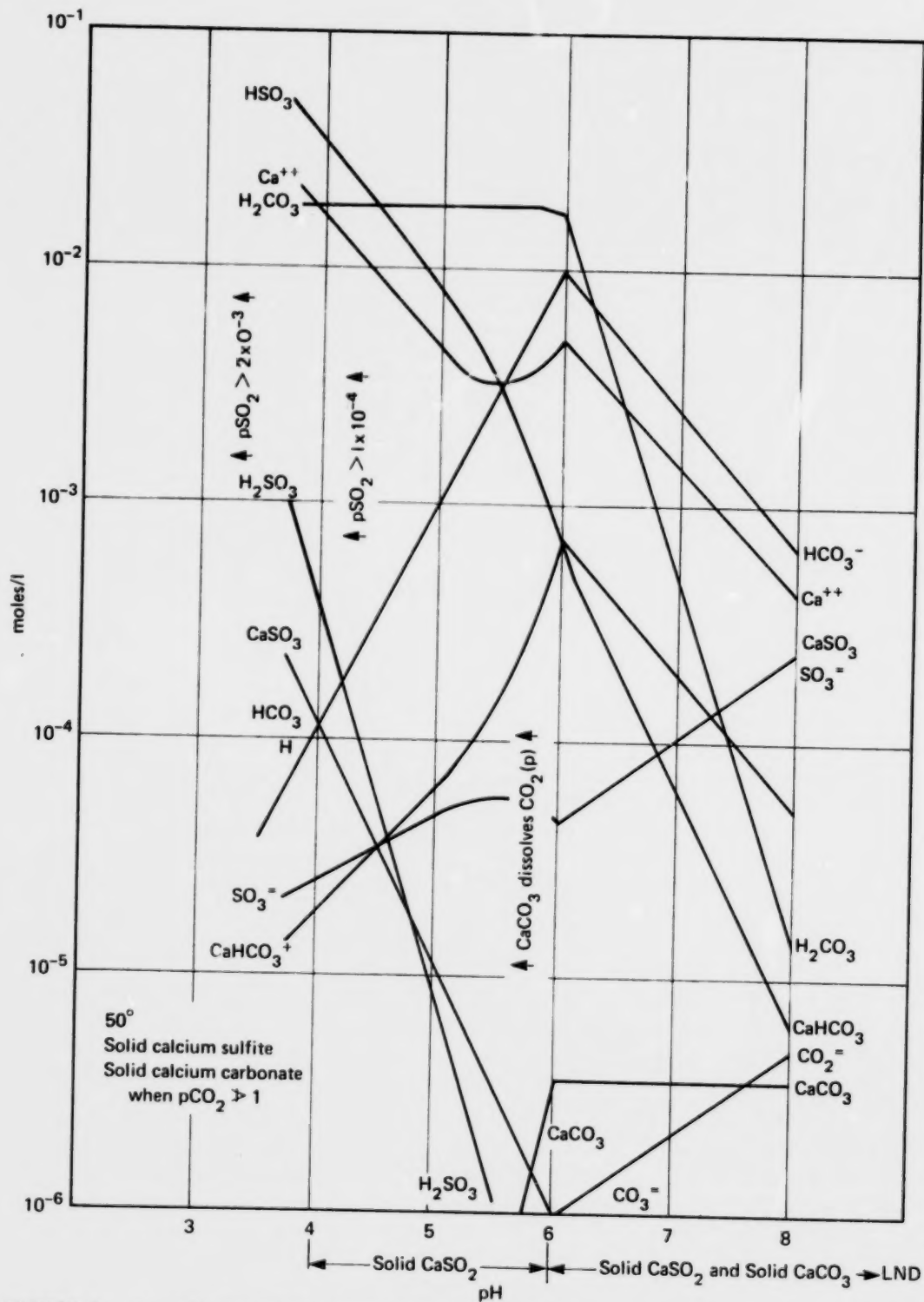


FIGURE 3. CARBONATE OF ALL IONIC SPECIES IN A SULFITE, CARBONATE SLURRY SYSTEM

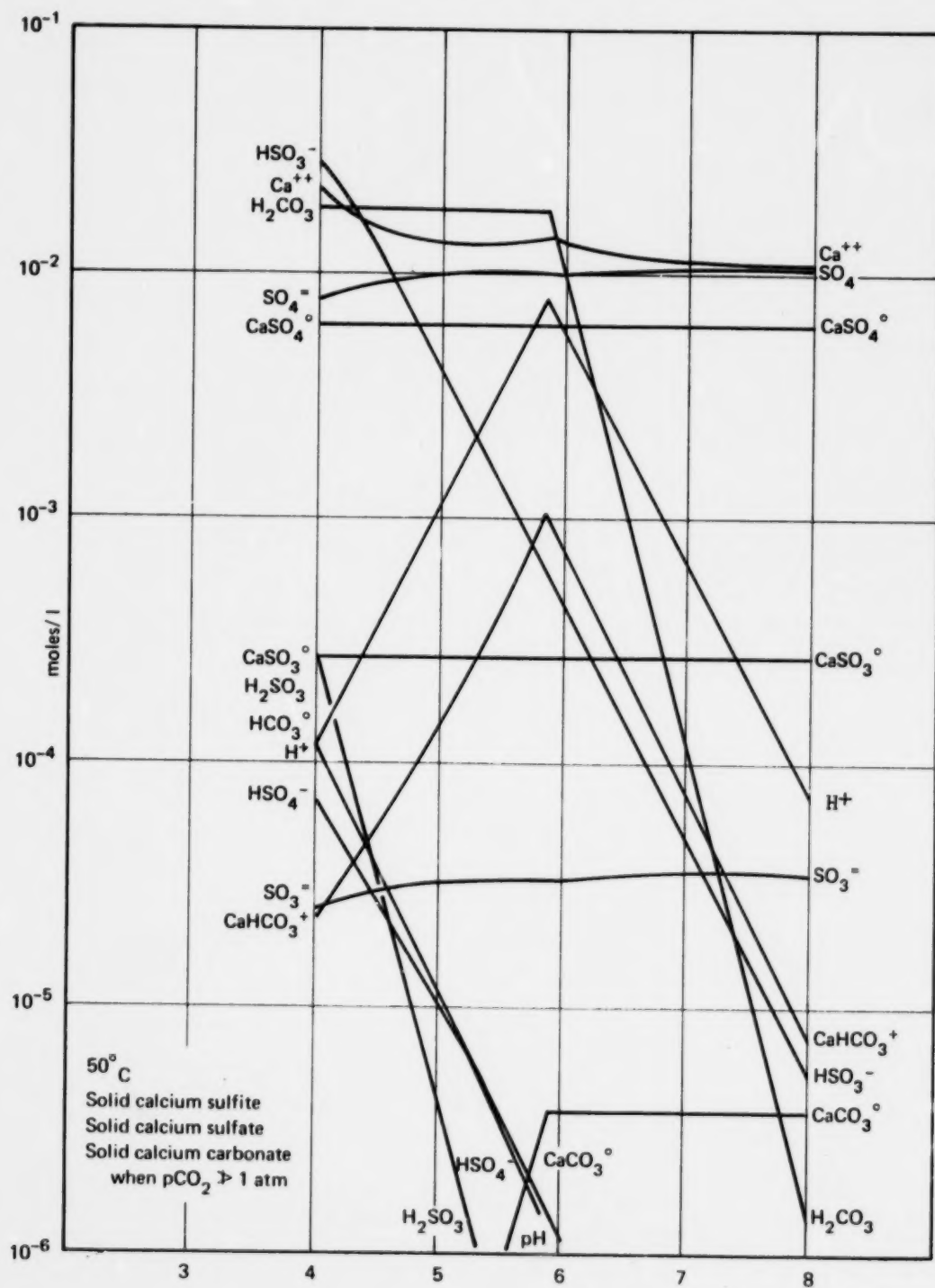
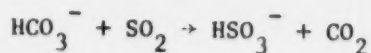


FIGURE 4. CONCENTRATIONS OF ALL IONIC SPECIES IN A SULFITE, SULFATE, CARBONATE SLURRY SYSTEM

these equilibria apply - particularly those of Figure 4 where solid sulfate is present in the slurry and/or on scaled surfaces. As the slurry circulates in the scrubber, it experiences pH changes on the average, and in localized areas. For example, the slurry emerging from the gas contactor is slightly more acid than that entering at the top, representing a shift to the left on Figures 3 and 4. The associated changes in concentration of the ionic species can readily be appreciated.

While it is more productive to discuss specific phenomena with respect to these data, we can make some general observations about scaling and about scrubber operation:

1. The evolution of CO_2 and loss of solid calcium carbonate at pH of about 5.9 effectively "buffers" the system at this pH. Many scrubbers, when operating at relatively low stoichiometries, reach this pH, particularly in the effluent from the gas-contacting region.
2. If the pH falls below this value and equilibrium is approached, all solid calcium carbonate will be lost, and solid calcium sulfite will begin to be dissolved. This suggests a method of scale control. Under normal circumstances, it will be desirable to operate at relatively high stoichiometries and pH where scrubber efficiency is high; but in this region, scaling can be expected due to the simultaneous precipitation of calcium sulfite and calcium sulfate. Calcium carbonate may also appear in the scale due to entrainment. If the stoichiometry is lowered or the L/G reduced, the pH may be permitted to fall below 5.8 where calcium sulfite (and, of course, any calcium carbonate) is dissolving. Referring to Figure 2, we see that solid calcium sulfate will be relatively nonprecipitating between pH = 5.9 and pH = 5.0, but will be precipitating if the pH falls below this. Thus, a potentially promising scale control method may be to let the pH take occasional excursions to a value approaching but not less than 5. Such a method is rather analogous to the acid treatments used for alkaline scale control in evaporators.
3. If, under some circumstances, a significant reaction step in the kinetic sequence occurs between dissolved species, we can choose appropriate candidates from Figure 4 and see how their concentration varies with pH. The reaction of bicarbonate ion with SO_2 or H_2SO_3 :

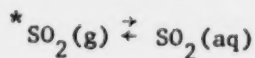


has been proposed as a rate-limiting step in the kinetic sequence. Figure 4 shows that the concentration of bicarbonate rises rapidly as the pH increases to about 5.9; at still higher pH, it falls again. This is compatible with the observation that scrubber efficiency rises as the pH rises, at least up to pH = 5.9. (Of course, other mechanisms may also explain this. For example, if interfacial diffusion of SO₂ into the liquid phase were rate-limiting, which it clearly is at very low pH values, then we would again expect scrubber efficiency to increase with pH: the partial pressure of SO₂ above the scrubber liquid falls as pH rises, and the driving force for SO₂ absorption increases.)

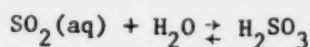
4. Noted on Figures 3 and 4 are the pH values at which the pSO₂ above the slurry reaches typical scrubber values and at which no further absorption would take place. In Figure 4, pSO₂ reaches 1×10^{-4} and 2×10^{-3} atmospheres at pH = 4.4 and 3.7, respectively.

KINETICS IN WET LIMESTONE SCRUBBING

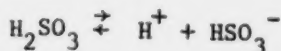
There is still considerable controversy concerning the principal chemical reactions that control absorption efficiency and scaling in a limestone wet scrubber. The following highly simplified set of reactions may serve as a convenient starting point for discussion.



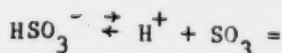
(1)



(2)

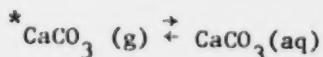


(3)

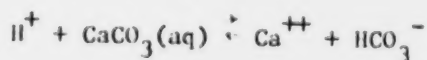


(4)

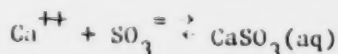
} SO₂ absorption



(5)

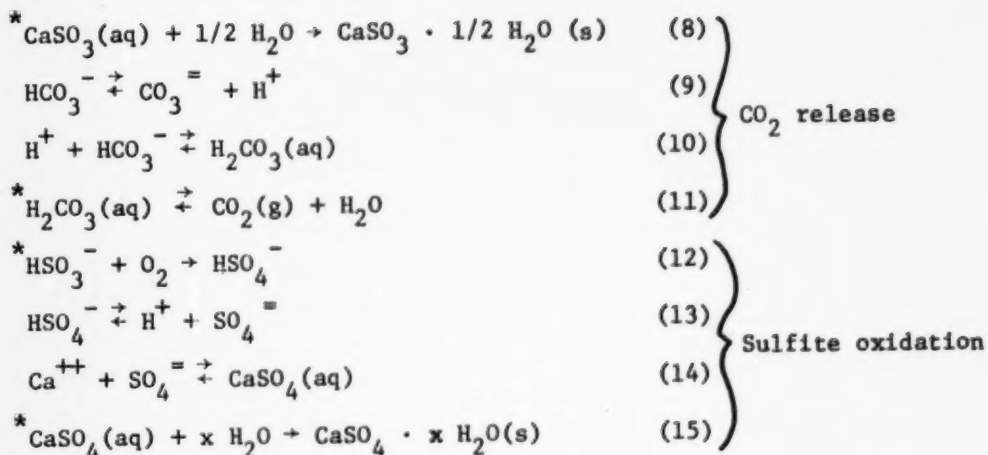


(6)

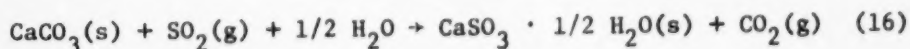


(7)

} CaCO₃ dissolution



The first ten equations describe the overall scrubbing reaction:



The last four equations describe the oxidation reaction, which ultimately can lead to precipitation of solid calcium sulfate.

The starred reactions are likely candidates for kinetic control. Equation (1) represents gas-liquid transfer for SO_2 . It would include diffusion of $\text{SO}_2(\text{g})$ to the gas-liquid interface, as well as transfer of SO_2 into the liquid phase and diffusion away from the interface. If the net transfer of SO_2 into the scrubber liquor is controlled to some extent by the solubility of the gas, which increases with decreasing temperature, removal of SO_2 from the flue gas should become more efficient as the temperature is reduced. Such an effect has been reported by TVA for gas inlet temperatures of 150-300°F (9). Once SO_2 has dissolved in the liquid phase, the equilibria (2) - (4) should be established very rapidly. In addition, the partial pressure of SO_2 in the liquid phase will reduce the driving force for SO_2 absorption. This partial pressure is increased as the pH falls; this is compatible with an observed reduction in scrubber efficiency, at low pH.

Equation (5) represents dissolution of $\text{CaCO}_3(\text{s})$ to form the neutral molecular species CaCO_3° or $\text{CaCO}_3(\text{aq})$. Reaction of dissolved CaCO_3° with H^+ , perhaps in the boundary layer surrounding each $\text{CaCO}_3(\text{s})$ particle, via Equation (6) would contribute to the carbonate dissolution process.

Equation (7) corresponds to an equilibrium among Ca^{++} , SO_3^- , and neutral CaSO_3° . Equation (8) represents the precipitation kinetics of $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}(\text{s})$. The higher the concentration of dissolved CaSO_3° , the more rapid may be the precipitation of solid. The concentration of CaSO_3° depends in turn on the activity product $[\text{Ca}^{++}][\text{SO}_3^-]$ for calcium and sulfite ions.

Equations (9) and (10) represent the various carbonate equilibria. The forward reaction in Equation (11) represents the release of $\text{CO}_2(\text{g})$ from the scrubber liquor; the backward reaction corresponds to transfer of CO_2 from the flue gas into the solution.

In summary, the general kinetic steps involved in the scrubbing of $\text{SO}_2(\text{s})$ from flue gas with CaCO_3 slurries are: dissolution of the gas in the liquid; dissolution of solid calcium carbonate; precipitation of $\text{CaCO}_3 \cdot 1/2 \text{H}_2\text{O}(\text{s})$; and evolution of $\text{CO}_2(\text{g})$ from the slurry into the vapor phase. Each of these general kinetic steps is mechanistically complicated. Furthermore, the individual steps are interrelated. Danckwerts(16) provided some data on gas-liquid transfer of sulfur dioxide and carbon dioxide, but most of the work has been confined to the alkaline range. Radian is exploring the precipitation kinetics of calcium sulfite using a CSTR(17). The dissolution kinetics of solid calcium carbonate has been studied to some extent by EPA. From the point of view of scaling, the precipitation kinetics are ultimately critical, although they depend upon the multitude of other kinetic and equilibrium steps occurring. While precipitation per se is not scaling, it can lead to scaling if it occurs on process equipment surfaces. Precipitation is a necessary component of the net wet scrubbing reaction, Equation (16). If it is not to lead to scaling, precipitation must be made to occur within the liquid phase, on the surface of seed crystals, or on surfaces outside of the scrubber loop. If the pH is carefully controlled, it should be possible to favor HSO_3^- over SO_3^- and hence to minimize the rate of calcium sulfite precipitation without too great an adverse effect on SO_2 removal efficiency.

On the other hand, oxidation is always a factor in limestone wet scrubbing, and as indicated in Equations (12)-(15), oxidation is believed to proceed through a HSO_3^- intermediate. Once HSO_3^- has been oxidized to HSO_4^- (Equation (12)), it will rapidly equilibrate with H^+ and SO_4^{--} . Interaction between Ca^{++} and SO_4^{--} can then lead to precipitation and/or scale of calcium sulfate. According to the phase diagram shown in Figure 5 for equilibrium sulfate precipitation, gypsum is the stable form below 100°F , while anhydrite is favored above 100°F .

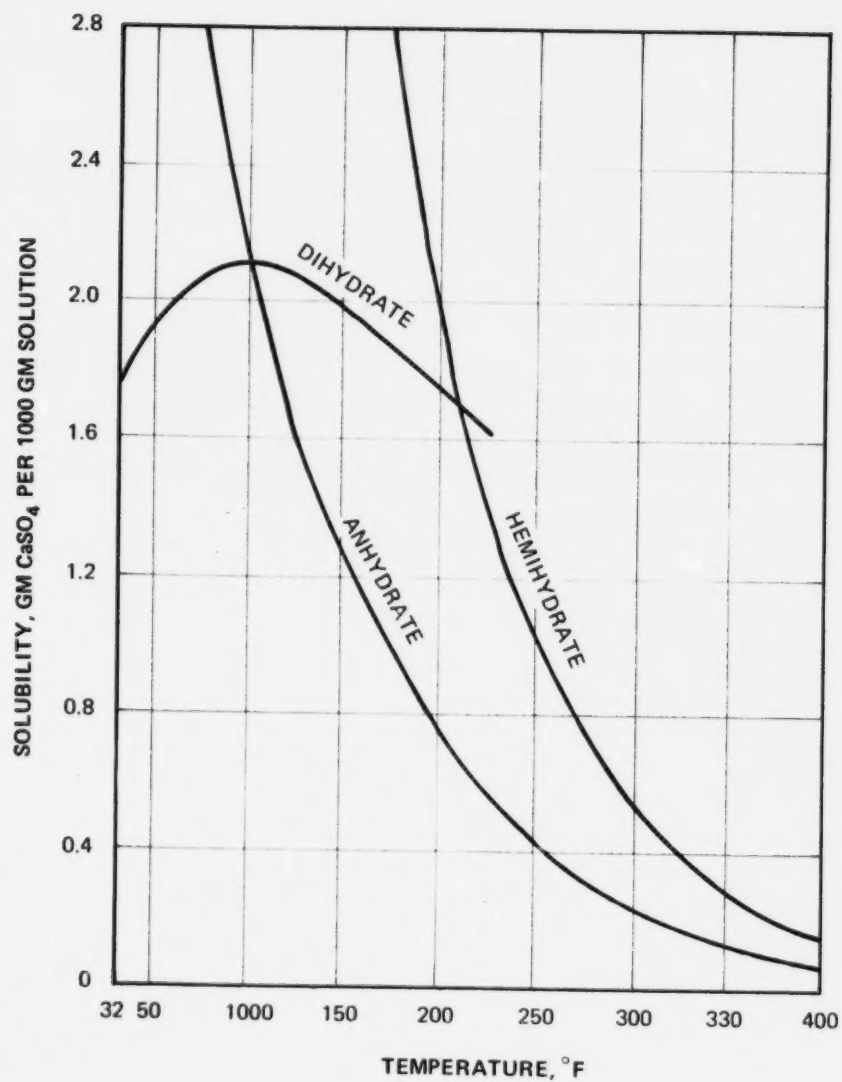


FIGURE 5. SOLUBILITIES OF THE SOLID PHASES IN THE CALCIUM SULFATE WATER SYSTEM

In many practical situations, it is the metastable hemihydrate which actually precipitates at the higher temperatures. In any case, precipitation of anhydrite or hemihydrate (plaster of paris) on process equipment surfaces can initiate a cementing reaction by conversion of the deposit to gypsum. The setting of plaster of paris (conversion of hemihydrate to gypsum), a reaction which occurs under water, could lead to catastrophic blockage if it occurs in the scrubber flow lines.

CHAPTER III

BENCH-SCALE SCRUBBER EXPERIMENTS

INTRODUCTION

The aim of the laboratory study is to define the mechanisms of scale formation in limestone based, wet scrubber systems. As indicated in the preceding chapter, the anticipated end products of the scrubbing reaction are known to be potential scale forming compounds. Therefore, the complex chemical kinetics of all vapor-liquid-solid reactions occurring in the scrubber have direct bearing on the scaling problem, and identification of the elementary rate controlling reactions may hold the key for any approach to circumvent scaling conditions by process modifications. Scaling reactions and SO_2 removal reactions must be considered in parallel, not only because some of the critical reaction steps are likely to be common to both phenomena, but also because acceptable solutions to the scaling problem may affect removal efficiency.

The bench-scale scrubber was designed so that individual potential scaling reactions might be isolated and studied in terms of scrubber operating parameters. In particular, the proportions of SO_2 , O_2 and CO_2 in the gas phase, as well as the amounts of CaCO_3 , CaSO_3 , and CaSO_4 in the scrubber liquor can be varied at will from zero to any desired level. The design parameters were selected to permit as close a simulation as possible to other small-scale scrubbers described in the literature. A packed-bed absorption column was selected as representative of the worst scaling situation, but sufficient flexibility was introduced into the apparatus design so other types of absorber might readily be substituted as appropriate.

EXPERIMENTAL APPARATUS

The schematic diagram shown in Figure 6 identifies the major components of the bench-scale apparatus. Gas with a constant inlet SO_2 concentration of 2,000 ppm passes once through the scrubber. The exit sulfur dioxide concentration is monitored continuously with a MSA infrared analyzer. Liquid inventory in the scrubber circuit is about 5 gallons with most of the liquid being contained in the hold tank immediately beneath the scrubbing column. At high liquid recycle rates examined, the liquid phase in the equipment approximates a well mixed reactor. The make up and purge streams are pumped at the same rate and simulate solids removal and addition of fresh absorbent. Analysis of the purge stream gives the stationary composition in the apparatus under well mixed conditions.

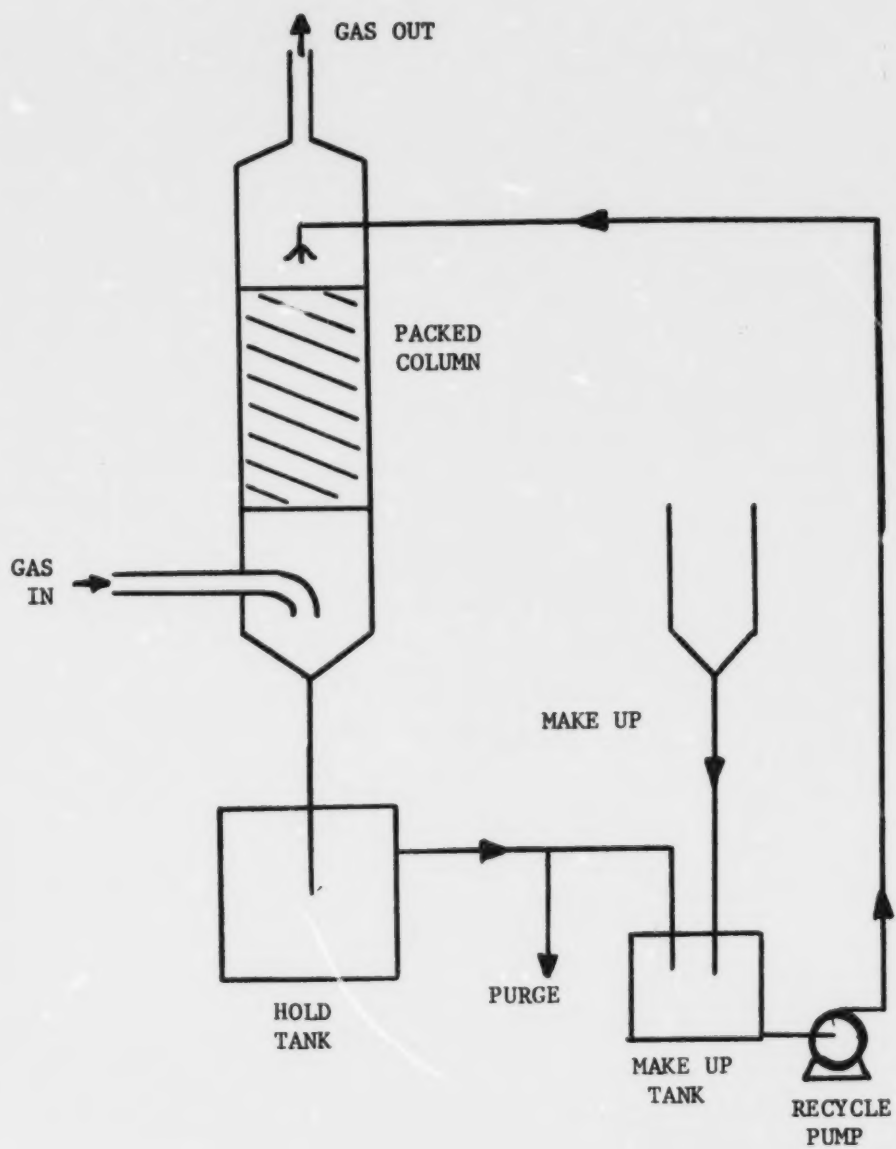


Figure 6. Line Diagram of Experimental Scrubbing Apparatus

Design Parameters

The design parameters were evolved from a consideration of several other scrubbers with varying characteristics described in the literature (Table VII). The ADL unit is most closely modeled on the Cottrell packed scrubber but has a lower linear gas velocity in the absorber and a lower liquid loading (gpm/ft^2). However, the comparable values for the TVA spray tower suggest that these lower figures are acceptable. The ADL unit provides for variation in the major experimental parameters over the following ranges: gas flow rate, 1 to 10 scfm; liquid recycle flow rate, 0.2 to 2 gpm; L/G ratio, 20 to 200 $\text{gpm}/1000 \text{ ft}^3$; scrubber liquid temperatures, 100° to 150°F ; gas temperatures, 250° to 300°F .

Absorption Column

The absorption column and much of the associated liquid recycle system is constructed of industrial glass from commercially available sections which are bolted together. This has the advantage of flexibility if modifications in apparatus design are required. The transparency of glass allows direct visual observation of any scale formation on the apparatus and on specimens of various test materials placed inside the apparatus. The smooth glass surface probably helps to minimize scale formation on the apparatus and facilitates removal of any deposits formed.

The column is operated under countercurrent flow. Hot gas enters at the base and liquid is pumped through a liquid distributor at the head of the column. All of the experiments reported to date have used a 4-inch diameter column and a 1 foot packed length of $1/2$ " Intalox saddles. Alternate packing materials, including $1/4$ " saddles, $1/4$ " and $1/2$ " rushing rings, and $1/4$ " glass spheres are available, but have not been employed to date. The absorption column is built into the system in such a way that the packing size can be readily changed, extra sections can be used to increase the length, the diameter can be changed or the packing can be replaced with a sieve tray or other configuration, as required.

Gas Handling System

The gas handling system allows various components of a typical flue gas, i.e., nitrogen, oxygen, carbon dioxide, and sulfur dioxide to be mixed together as desired. Two liquid nitrogen cylinders in series allow flow rates of up to 10 scfm to be achieved. The mixed gases are passed through an electrically heated packed tube and gas temperatures of 300°F at 10 scfm can be attained readily. Gas temperature at the scrubber inlet is maintained with a temperature controller attached to the furnace and operated by a thermocouple in the exit gas stream. Gas flow rates are measured by rotometers, except for the SO_2 which is metered with a mass flow controller.

Table VII. Design Parameters for Several Scrubbing Units

Parameter	ADL packed bed (Bench unit)	Cottrell packed bed (pilot unit)	TVA TCA (pilot unit)	TVA spray tower (Bench unit)	EPA (pilot unit)
Gas flow scfm	11.2	1000	2000	8	200
Recycle liquid flow gpm gpm/ft ²	0.45 5.2	40 28.4	96 34	0.64 7.3	8.4 19
L/G gpm/1000 ft ³	40	40	48	80	42
Cross section area ft ²	0.087	1.41	2.8	0.087	0.44
Volume ft ³	0.087	7.05	42	0.19	3.52
Linear gas velocity ft/sec	2.1	10.7	12.5	1.5	6.6
Gas residence time (secs)	0.4	0.42	1.3	1.4	1.2

Liquid Handling System

Liquid or slurry from the absorber falls into a stirred, 5 gallon spherical glass vessel which serves as the delay vessel or hold tank. The residence time in the hold tank can be varied between 1 to 10 minutes by adjustment of the liquid recycle rate and the liquid volume (controlled by the height of the overflow to the mixing tank). After leaving the hold tank, a proportion of the liquid flow is purged through a sampling system for chemical analysis.

The remainder of the liquid stream enters the 1 gallon stirred mixing tank, where fresh slurry feed is added before recycling the liquid stream to the absorber. Residence in the mixing tank can be varied from about 30 seconds to 3 minutes. From the mixing tank, the slurry is recycled through the pump and a flow meter back to the absorber, or through a bypass loop directly into the hold tank if it is required to take the absorption column out of service without interrupting the recycle operation.

The flexible impellor recycle pump will pump up to about 5 gallons a minute against the head (about 8 ft) in the apparatus. Lower liquid recycle rates are achieved by reducing the pump speed and throttling the outlet from the pump. Before installation, this pump was tested with a 10% slurry of calcium carbonate which it was able to pump for several hours without any noticeable solids build up or variation in flow rate.

The experimental unit does not have any solids separation facility. This effect can be simulated by variation of the purge and fresh feed makeup flow rates and by control of the chemical composition of the fresh feed slurry.

ANALYTICAL PROCEDURES

An on-line MSA infra-red analyzer was used to monitor $\text{SO}_2(\text{g})$ in the inlet and outlet gas streams.

The inlet slurry (makeup line) was analyzed for pH and total calcium. The outlet purge stream from the hold tank was analyzed as required for pH, (on-line) total sulfite, sulfite in solution, total calcium, calcium in solution, total sulfate and sulfate in solution. For each sample, an aliquot of the slurry was analyzed for total calcium and total sulfite by the methods described below. The slurry was allowed to settle and a second sample taken of the clear solution for determination of calcium and sulfite in solution. A sulfite balance was obtained by comparing the SO_2 removal at a given makeup rate with the total sulfite in the slurry of the purge sample. Similarly the calcium balance was obtained from the difference between the total calcium concentration in the slurry makeup and the total calcium in the purge sample.

To determine total sulfite (sulfite and bisulfite) in solution or slurry (total oxidizable sulfur) a standard iodometric technique is used. This involves addition of the sample to excess iodine in acetic acid followed by back titration with standard thiosulfate solution. The variation recommended in the Radian report (Technical Note 200-004-04, David W. DeBerry, May 22, 1970) uses buffered iodine solution (pH 6 to 6.2) with back titration with arsenite solution to avoid interference from nitrite ions. Since nitrite ions were not present in any of our solutions, the standard technique proved more convenient. This procedure effectively measures the concentration of bisulfite ion in solution because the amount of sulfite ion in solution is very small.

Calcium in solution is measured by standard atomic absorption techniques.

Calcium in the slurry is measured by the following volumetric titration against EDTA solution. A convenient aliquot (equivalent to about 40 mgs Ca) is diluted with 50 mls of water and dissolved by the addition of 10% HCl. The solution is then made alkaline by the addition of 30 mls, 0.5 N, NaOH (or KOH). A mixed indicator is then added and the solution titrated against 0.1 molar EDTA, sodium salt, which, at the end point, changes the solution from pink to purple. The mixed indicator used is compounded from 20 grams of NaCl, 0.1 grams of calcein and 0.04 grams of murexide; about 0.2 mg is used for each titration.

Total sulfate in solution or slurry was determined by a gravimetric procedure involving acidification with HCl, precipitation with BaCl₂, filtration, and finally ignition of BaSO₄.

Solids Collection

A sampling check made early in the program showed that the concentration of solids in the purge stream was the same as the solids concentration in the hold tank. Subsequently all the analytical samples were taken from the purge stream. Solids are collected, if desired, by vacuum filtration of known volume of slurry through a previously tared fritted glass gooch crucible with a medium porosity filter. The solid is then dried overnight at 105°C and weighed. In most of the experimental work, it was found simpler and more accurate to obtain a mass balance by measuring slurry and supernatant liquor compositions, as described above, without filtration of the solids.

Carbonate and Bicarbonate.

No carbonate analyses were made under the present program, since the concentrations can be calculated quite accurately by combining equilibrium thermodynamic analysis with the measured chemical properties of the system.

PRELIMINARY SHAKEDOWN EXPERIMENTS

The first experiments were carried out to study the absorption of sulfur dioxide into water and into 0.2 N sodium hydroxide to determine the lower and upper limits of scrubber efficiency. Results are summarized in Tables VIII and IX. These experiments with sodium hydroxide and water are meant to indicate the areas where gas and liquid mass transfer resistance respectively should be the rate-controlling step. Absorption efficiencies of carbonate or sulfite slurries should fall between these two extremes.

Water (Table VIII) shows a low SO₂ removal efficiency, reaching only 42.5% at low gas rates and very high liquid rates. The pH measured indicates that the solution is close to the thermodynamic equilibrium.

Results with sodium hydroxide (Table IX) contrast markedly with those for water. Scrubbing efficiencies approached 100% except at very high gas flow rates. Changing the liquid rate to the column has little effect on the removal efficiency. As shown in Figure 7, SO₂ removal is proportional to the gas flow rate indicating that the gas phase resistance is rate controlling for NaOH solution at pH 12.

Data obtained for slurries of 5% calcium sulfite, 5% calcium carbonate, 2% calcium carbonate and 1% calcium carbonate are summarized in Tables X-XIII. Each slurry composition was studied as a function of liquid recycle rate and liquid make up rate. Most of the data were obtained at a liquid temperature of 100°F, although some preliminary data was also obtained at 117°F.

The effect of changes of L/G [gpm per 1,000 ft³] on the conversion efficiency for SO₂ with the various scrubbing liquors studied is shown in Figure 8. All the results refer to the same gas rate, 5 SCFM. It can be seen that the 1, 2 and 5% slurries with excess carbonate can approach the removal efficiency of NaOH - with a negligible L/G effect. In contrast the results for 0.5% calcium carbonate show a marked dependence on L/G ratio. The results fall between those for calcium carbonate and calcium sulfite slurries showing that L/G has a more pronounced effect at lower stoichiometry. Under the same conditions, the 5% calcium sulfite slurry has a conversion efficiency of about 30%, which is not much higher than water. These trends reflect a basic chemical difference between the two groups. Reaction with sodium hydroxide and calcium carbonate is essentially irreversible and absorption at the interface (or the gas phase resistance) becomes rate controlling. Reaction with calcium sulfite and water leads to a true equilibrium (as opposed to steady state) concentration of bisulfite ion in solution. The pH at steady state, for example, under the reaction conditions examined, indicates that the liquid phase for water and calcium sulfite slurries is very close to the thermodynamic equilibrium concentrations.

Table VIII. Summary Results--Scrubbing Liquid, Water

Inlet SO₂ concn 2000 ppm
Initial pH 7.5

gas temp 275° F
liq. temp 100° F

N ₂ flow scfm	pH	SO ₂ out ppm	Feed rate gph	Recycle gpm	L/G	SO ₂ removed % mols/hr ft ²	
5	2.55	1750					
5	2.48	1550	1.6	0.9	180	12.5	1.0
5	2.45	1600	7.0	0.9	180	22.5	1.8
5	2.45	1600	7.0	1.36	372	20	1.6
5	2.40	1600	8.2	1.36	372	20	1.6
5	2.43	1500	8.2	0.4	80	20	1.6
			10.0	0.4	80	25	2.0
5	2.42	1850	1.6	1.36	372	7.5	0.6
3	2.45	1850	1.6	1.36	450	7.5	0.36
3	2.52	1500	1.6	1.36	450	20	0.96
3	2.50	1150	6.6	1.36	450	42.5	2.05
2	2.45	1250	6.6	1.36	680	37.5	1.20
2	2.4	1250	6.6	0.9	450	37.5	1.20
2	2.43	1200	6.6	1.88	940	40	1.28
2	2.45	1150	8.4	1.88	940	42.5	1.36

Table IX. Summary Results--Scrubbing Liquid: Sodium Hydroxide

Initial pH 12.8
Inlet SO₂ 2000 ppm

NaOH conc 0.2N
Gas temp 275° F
Liq. temp 100° F

N ₂ flow scfm	pH	SO ₂ out ppm	Make up rate gph	Recycle gpm	L/G	SO ₂ removed % mols/hr ft ²	
5	12.8	< 50					
7.8	12.65	< 50	0.87	0.9	180	>97.5	> 7.9
7.6	12.53	50	0.87	0.9	115	>97.5	>12.1
7.4	12.4	75	0.87	0.4	52	97.5	12.0
(10.0	8.9	200	0.87	0.26	35	96	11.5
10.0	5.9	400	2.86	0.26	26	90	14.6)
					26	80	13.0

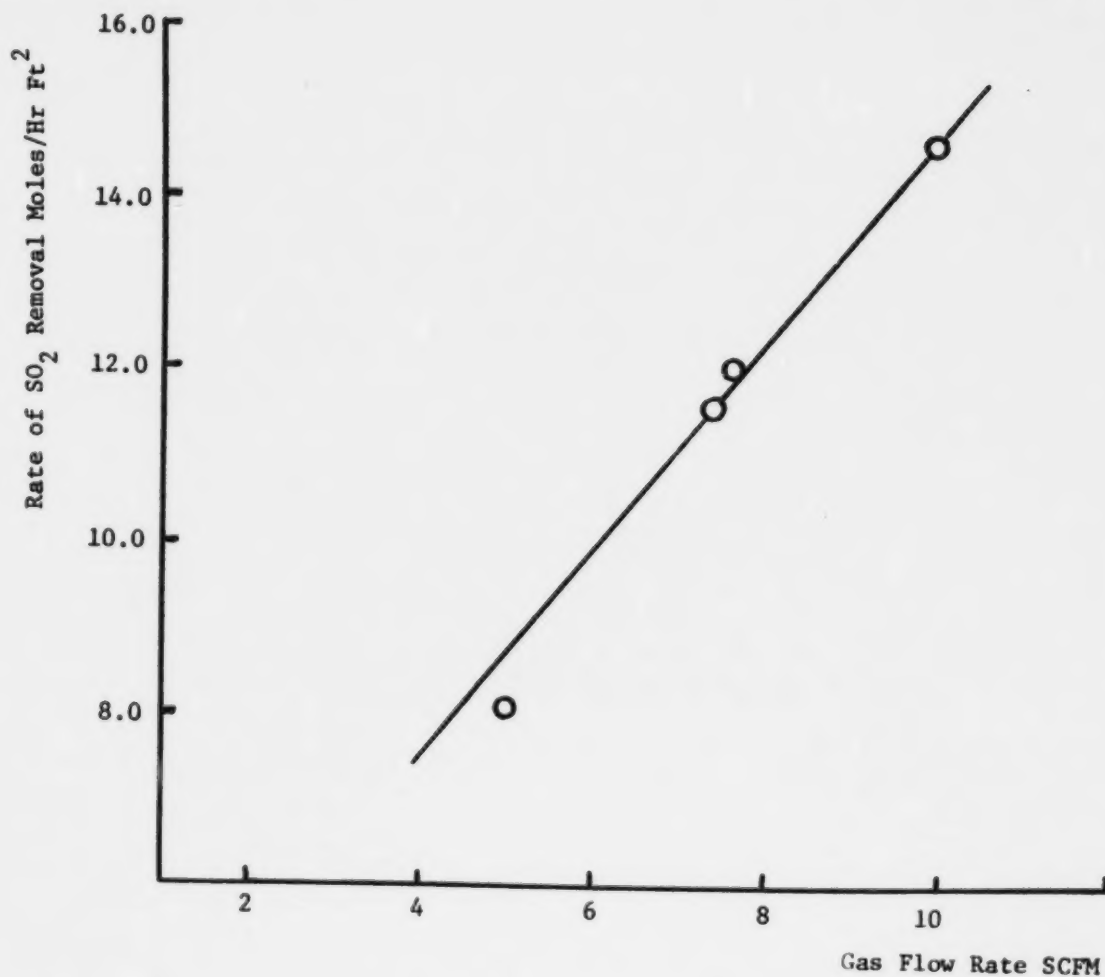


Figure 7. Sulfur Dioxide Removal With NaOH as a Function of Gas Rate.

Table X. Summary Results--Scrubbing Liquid, 5% CaSO₃ Slurry

N₂ 5 scfm
Inlet SO₂ 2000 ppm
Initial pH 8.1

Liq. Temp 100° F
Gas Temp 255° F

pH	SO ₂ out ppm	Make up gph	Recycle gpm	L/G	SO ₂ removed ² % mols/hr ft	
5.2	250	1.6	0.9	180	87.5	7.0*
4.35	550	1.6	0.9	180	72.5	5.8*
3.9	1375	1.6	0.9	180	31	2.5
3.8	1600	1.6	0.4	80	20	1.6
3.83	1450	1.6	0.26	51	27.5	2.2
3.9	1330	2.8	0.4	80	33.5	2.7
Temp. inc to 115° F						
4.0	1500	1.6	0.4	80	25	2.0
3.95	1500	1.6	0.9	180	25	2.0*
4.03	1200	1.6	0.26	51	40	3.2
4.03	1150	2.8	0.26	51	42.5	3.4

*Not steady state

Table XI. Summary Results--Scrubbing Liquid 5% CaCO₃ Slurry

N₂ rate 5 scfm
Initial pH 8.5
Inlet SO₂ 2000 ppm

Gas temp 275° F
Liq. temp 100° F

pH	SO ₂ out ppm	Make up mls/min gph		Recycle gpm	L/G	SO ₂ removed ² % mols/hr ft	
6.6	150	190	3.0	1.0	200	92.5	7.4
6.5	180	190	3.0	0.5	100	91	7.25
6.4	200	190	3.0	0.25	50	90	7.2
6.7	150	190	3.0	1.0	200	92.5	7.4
6.72	130	116	1.8	1.0	200	93.5	7.5
6.77	200	450	7.1	1.0	200	90	7.2
6.78	200	62	1.0	1.0	200	90	7.2

Table XII. Summary Results--Scrubbing Liquid 2% CaCO₃ Slurry

N ₂ rate 5 scfm SO ₂ 2000 ppm Initial pH 8.6				Gas temp 275° F Liq. temp 100° F			
pH	SO ₂ out ppm	Make up		Recycle gpm	L/G	SO ₂ removed	
		mls/min	gph			%	moles/hr ft ²
6.65	180	192	3.0	1.0	200	91	7.25
6.6	180	192	3.0	0.5	100	91	7.25
6.53	230	192	3.0	0.25	50	88.5	7.1
6.7	100	192	3.0	1.0	100	95	7.6
6.72	130	114	1.8	1.0	100	93.5	7.5
6.72	100	464	7.3	1.0	100	95	7.6
6.73	130	62	1.0	1.0	100	93.5	7.5
Temp increases 117° F							
6.72	140	192	3.0	1.0	100	93	7.5
6.62	160	192	3.0	0.5	150	92	7.4

Table XIII. Summary Results--Scrubbing Liquid 1% CaCO₃ Slurry

N ₂ rate 5 scfm SO ₂ 2000 ppm Initial pH 8.2					Gas temp 275° F Liq. temp 100° F			
Experiment	pH	SO ₂ out ppm	Make up		Recycle gpm	L/G	SO ₂ removed ²	
			ml/min	gph			%	mols/hr ft
1	6.58	190	190	3.0	1.0	200	90.5	7.25
2	6.5	240	192	3.0	0.5	100	88	7.05
3	6.45	310	192	3.0	0.25	50	84.5	6.75
4	6.6	185	192	3.0	1.0	200	91	7.3
5	6.62	185	100	1.6	1.0	200	91	7.3
6	6.63	185	476	7.5	1.0	200	91	7.3
7	6.7	205	50	0.8	1.0	200	90	7.2

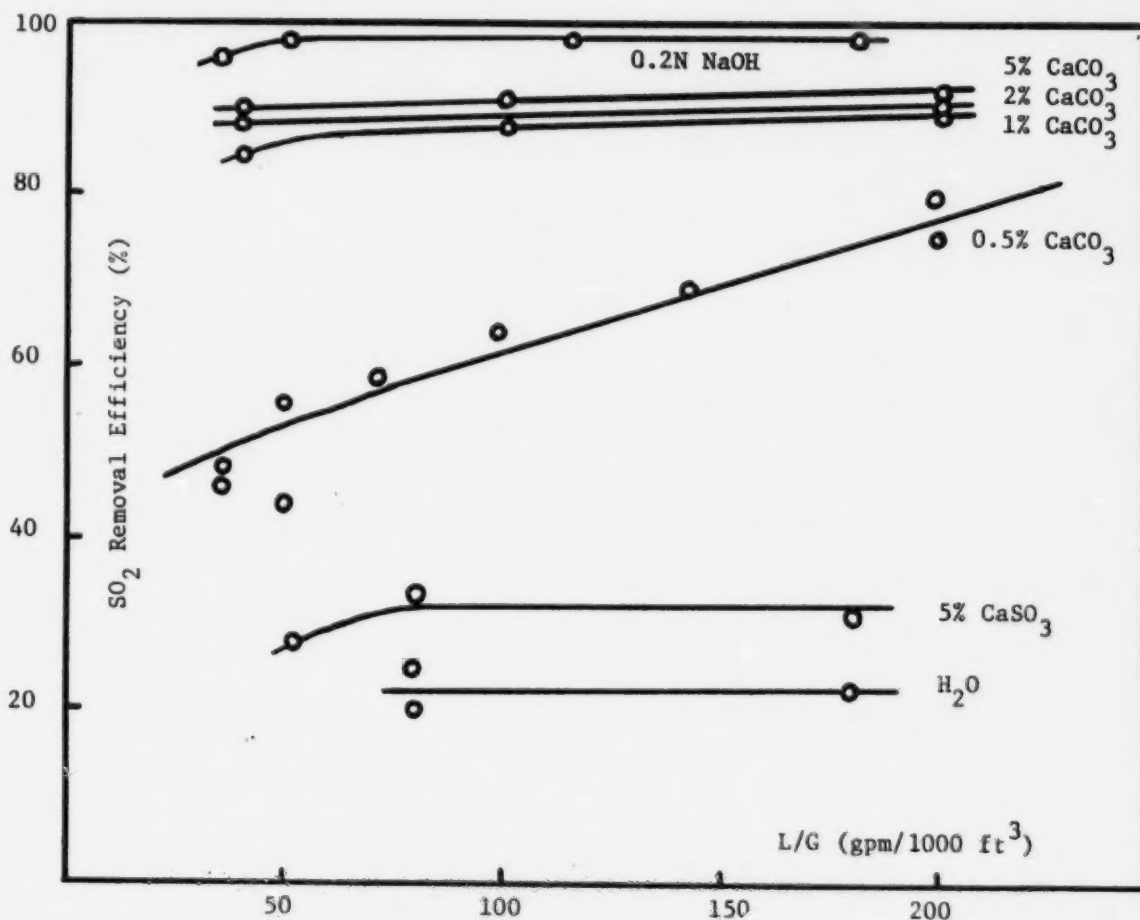


Figure 8. Sulfur Dioxide Removal as a Function of Liquid to Gas Ratio for Different Scrubbing Agents (100°F)

Therefore, the rate of removal of sulfur dioxide by calcium sulfite or water is limited by diffusion in the liquid phase (liquid phase resistance) with the gas liquid interface being essentially at equilibrium. Removal rates for sulfite slurries are higher than for water because the solution has a higher absorption capacity.

This is confirmed in Figure 9 which shows the change in the sulfur dioxide removal efficiency as a function of time, from the initial introduction of sulfur dioxide into the scrubber until a steady state conversion is achieved. Extrapolation of the results back to time zero shows that initially, the SO_2 removal efficiencies of water, calcium sulfite and calcium carbonate for SO_2 approach a common value corresponding to the gas phase resistance. For water and sulfite slurries the driving force diminishes with time as the liquid phase approaches equilibrium.

COMPARISON WITH OTHER SCRUBBERS

A comparison of our data with that reported in the literature for SO_2 absorption in limestone slurries is given in Figures 10 and 11. The agreement is generally good, particularly for the low to medium velocity scrubbers.

It may be noted that the effect of L/G on SO_2 removal becomes less important as L/G increases for the low velocity scrubbers. Our scrubber simulates the performance of the two-stage TCA (at 12.6 fps) perfectly at all L/G values up to at least 80. At L/G = about 90-100 it also gives a good simulation of the Venturi-rod spray tower and the medium velocity (Ontario Hydro) spray tower. The data on high velocity (multi-grid) and large surface (3-stage TCA) types show that our data has only limited applicability to those cases. Thus our scrubber is limited by gas velocity (or mass transfer surface area) at high L/G values, and flow rates of 5 scfm. Between L/G = 32 to 48 our scrubber does simulate the operation of a multi-grid scrubber with a gas velocity of 13.5 fps (see Figure 12).

TEST PROGRAM

After completion of the initial shake-down runs described above, a systematic series of experiments was carried out to isolate some of the reactions that have been postulated as contributing to scrubber efficiency, and to determine the effect of these reactions on scale formation. The test program was designed to evaluate the separate and interacting effects of L/G, stoichiometry (or pH), temperature, and degree of oxidation on SO_2 absorption and scaling for CaCO_3 , limestone, and CaSO_3 slurries. The levels of the experimental parameters investigated are summarized in Table XIV.

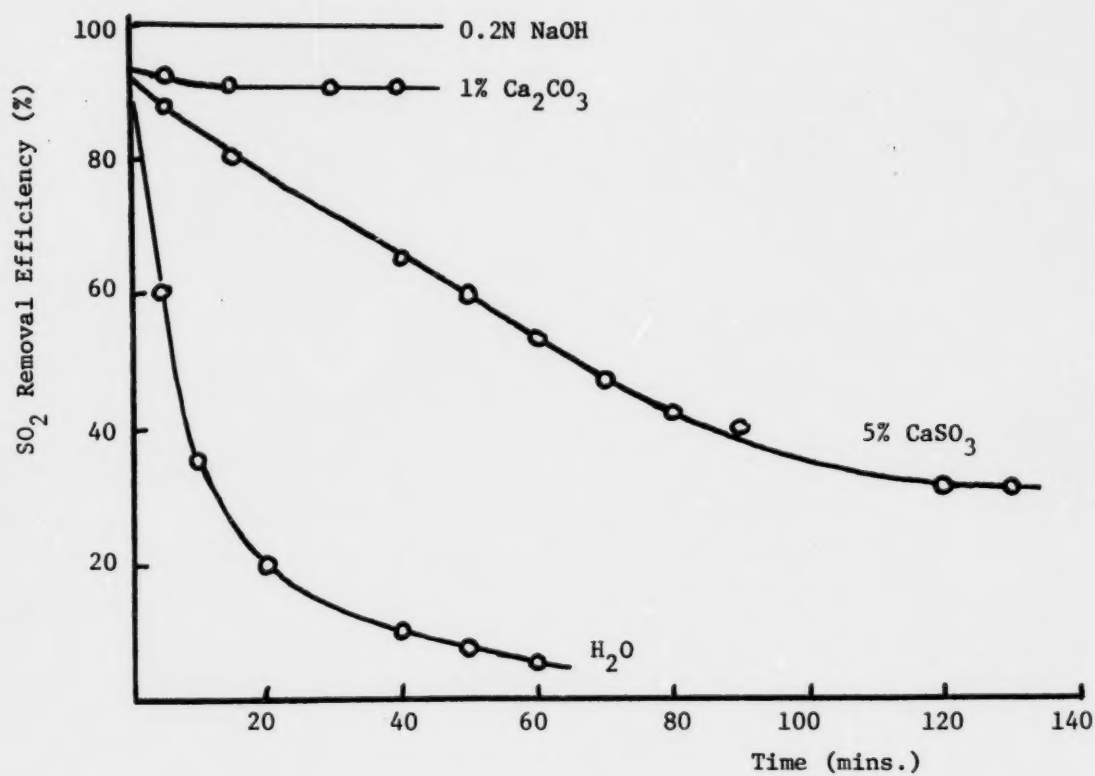


Figure 9. Change in Sulfur Dioxide Removal Efficiency With Time After Startup

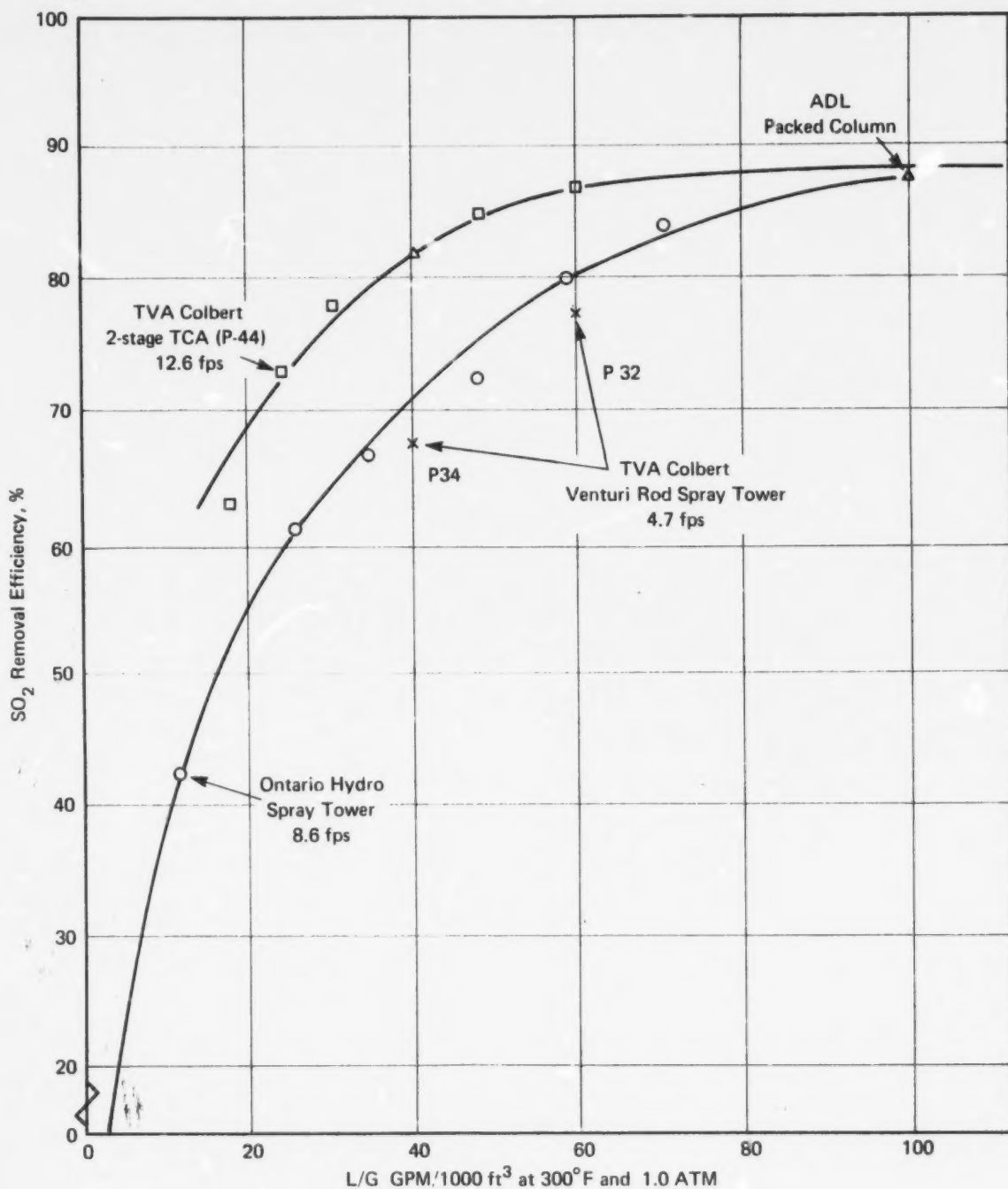


FIGURE 10 COMPARISON OF EFFECT OF L/G ON SCRUBBER EFFICIENCY – MEDIUM SURFACE (VELOCITY) SCRUBBERS

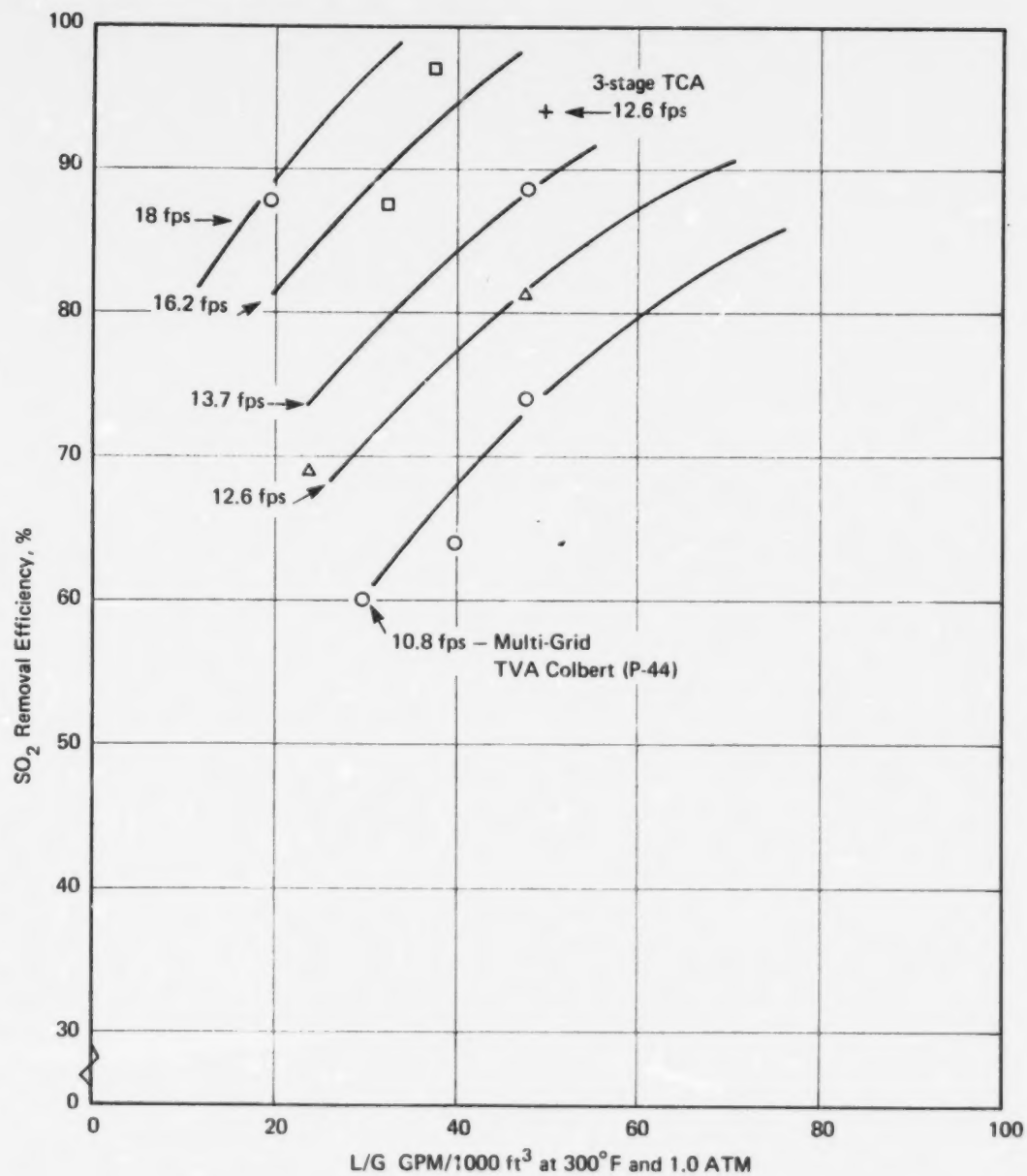


FIGURE 11. COMPARISON OF EFFECT OF L/G ON SCRUBBER EFFICIENCY - HIGH VELOCITY (SURFACE) SCRUBBERS

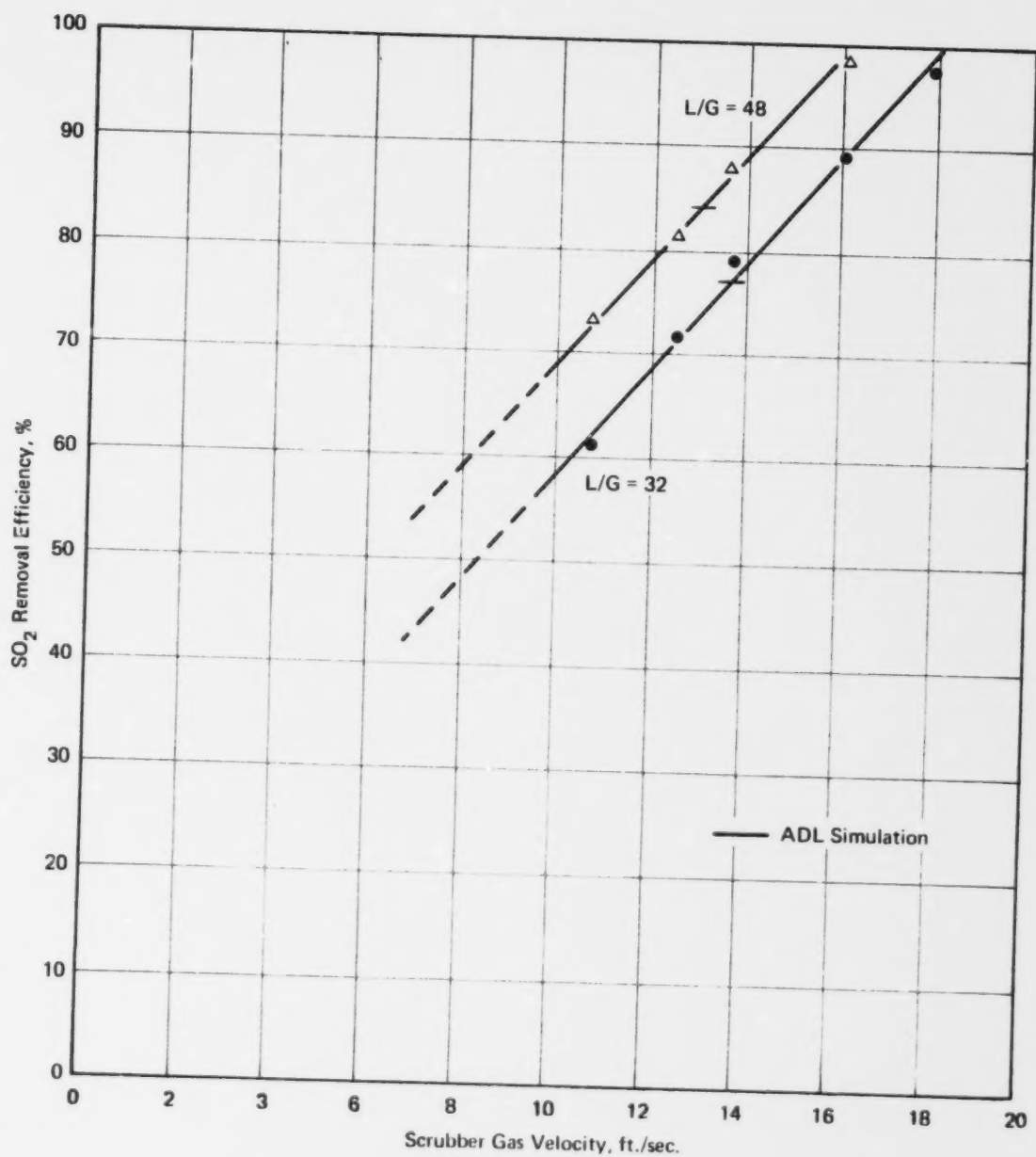


FIGURE 12 MULTI-GRID SCRUBBER – EFFECT OF GAS VELOCITY ON EFFICIENCY AT CONSTANT L/G

TABLE XIV

EXPERIMENTAL TEST PROGRAM

<u>Scrubbing Slurry</u>	<u>L/G</u>	<u>Stoichiometry</u>	<u>Slurry Temp.</u>
CaCO_3			
0.5%	50, 100	0.3 - 1.95	100, 125°F
1 %	50, 100	0.9 - 2.8	100, 125°F
Limestone			
0.6%	50 - 330	0.4 - 1.7	100, 125°F
CaSO_3			
0.5%	50 - 200	-	100, 125°F

Notes:

1. The SO_2 inlet concentration was 2,000 ppm in most experiments. Any deviations are noted in the text.
2. The N_2 flow rate has 5 scfm.
3. The gas temperature was 275°F.

RESULTS

0.5% Calcium Carbonate Slurries

Scrubbing Efficiency and Scaling in the Absence of Oxygen

Experimental runs with 0.5% calcium carbonate slurries are summarized in Tables XV-XVII. Results are plotted in Figures 13-18. In general, sulfur dioxide removal efficiency is higher at $L/G = 100$ than at $L/G = 50$ for a given pH and stoichiometry; and the effect is more pronounced at 125°F than at 100°F. At a given effluent hold tank pH, the removal efficiency is somewhat higher at 100°F than at 125°F, particularly at $L/G = 50$. A substantial pressure drop, indicative of significant sulfite scaling, was observed at 125°F, but not at 100°F.

In Figure 13, sulfur dioxide removal for 0.5% calcium carbonate at 125°F is seen to vary linearly with pH and to increase at the higher L/G ratio. In Figure 14, the results are plotted as a function of stoichiometry (proportional to make-up rate in our system). Removal efficiencies are seen to drop quite sharply below a stoichiometry of 0.8-0.9, corresponding to complete utilization of limestone consistent with a drop in pH below 5.8. The corresponding plots of removal efficiency as a function of pH and stoichiometry for runs made at 100°F are shown in Figures 15 and 16, respectively. Comparing Figures 13 and 14, we may note that at 100°F there is some increased SO_2 removal, less scatter in the data points, and a smaller L/G effect. The drop in removal efficiency below a stoichiometry of 0.9 is seen in both Figures 16 and 15 for the two temperatures investigated.

Under the conditions of run XV (0.5% $CaCO_3$, 125°F), increases in column pressure drop were noted after about 12 hours' operating time. Figure 17 indicates the pressure drops observed throughout the run. By the end of 23 hours, scaling in the lines leading to the pump and rotometer had become severe enough to shut down the system. In contrast, Figure 18 shows that there was no substantial pressure drop increase during 17 hours on line in run XVI, probably as a result of the lower liquid temperature (100°F-125°F for run XV).

1% Calcium Carbonate Slurries

Scrubbing Efficiency and Scaling in the Absence of Oxygen

Experimental runs with 1.0% calcium carbonate slurries are summarized in Tables XVIII and XIX. Results are plotted in Figures 19-23. At a given makeup rate, or stoichiometry, sulfur dioxide removal efficiency is higher at $L/G = 100$ than at $L/G = 50$. In contrast to results with the 0.5% $CaCO_3$ slurry, pH and removal efficiency change very little with stoichiometry, and no marked temperature effects were observed. The SO_2 removal rate again varied linearly with pH, but fell much more rapidly in the pH range of 6.8 to 6.5 than with the lower slurry concentration.

Table XV. Summary Results--Scrubbing Liquid, 0.5% CaCO₃

Initial pH 8.2		Gas Temp. 275° F					
Inlet SO ₂ 2000 ppm		Liquid Temp. 125° F					
N ₂ flow 5 scfm							
N ₂ oxygen							
Sample	pH	SO ₂ Out ppm	Make Up Rate gph	Recycle gpm	L/G	SO ₂ Removal %	Stoichiometry
22 - 1	4.63	1040	1.3	0.25	50	48	0.4
22 - 2	5.90	540	2.7	0.25	50	73	0.7
22 - 3	5.28	700	2.3	0.25	50	65	0.6
22 - 4	6.33	350	4.9	0.25	50	83	1.3
22 - 5	6.25	315	3.9	0.25	50	84	1.0
22 - 6	5.60	325	2.7	0.50	100	84	0.7
22 - 7	6.35	100	5.0	0.50	100	95	1.3
22 - 8	4.53	990	1.3	0.50	100	50	0.4
22 - 9	6.05	240	3.9	0.50	100	88	1.0
22 - 10	4.90	675	2.2	0.50	100	66	0.6

Sample	SO ₂ Removed m.moles/l	Sulfite by Titration		Sulfite Balance	Ca Inlet	Ca Exit		Calcium Balance	
		Total m.moles/l	Solution m.moles/l	m.moles/l	Total m.moles/l	Total m.moles/l	Solution m.moles/l	m.moles/l	
22 - 1	67.5	23.8	20.1	-43.7	52.5	18.5	15.5	-34.0	
22 - 2	48.0	22.7	5.5	-25.3	50.7	28.0	7.3	-22.7	
22 - 3	52.2	28.5	12.8	-23.7	51.0	28.5	10.5	-22.5	
22 - 4	30.8	23.5	.8	-7.3	50.0	38.8	7.3	-11.2	
22 - 5	38.9	28.3	1.6	-10.6	51.0	39.5	6.3	-11.5	
22 - 6	56.0	36.9	8.6	-19.1	51.0	43.5	6.8	-7.5	
22 - 7	34.7	31.4	.2	-3.3	49.7	47.5	5.0	-2.2	
22 - 8	68.3	45.7	26.5	-22.6	51.0	41.0	72.5	-10.0	
22 - 9	41.5	32.5	1.6	-9.0	50.0	41.0	5.3	-9.0	
22 - 10	54.3	42.8	15.3	-11.5	39.5	39.5	11.5	-11.0	
		Average -17.6				Average -14.2			

Table XVI. Summary Results--Scrubbing Liquid, 0.5% CaCO₃

Sample	pH	Initial pH 7.8		Gas Temp. 275° F		SO ₂ Out Ppm	Make Up Rate gph	Recycle gpm	L/C	SO ₂ Removal %	Stoich.	SO ₂ Removed m.moles/l	Sulfite by Titration	
		Inlet SO ₂ 2000 ppm N ₂ flow 5 scfm	NO oxygen	Liquid Temp. 100° F									Total m.moles/l	Solution m.moles/l
23 - 1	5.52	450			2.7	0.25	50		78	0.7		52.8	22.5	11.6
23 - 2	4.48	790			1.6	0.25	50		61	0.4		71.0	33.7	25.3
23 - 3	6.13	215			4.9	0.25	50		90	1.3		33.2	27.3	1.1
23 - 4	6.03	240			3.7	0.25	50		88	1.0		43.0	33.0	0
23 - 5	5.50	350			2.6	0.50	100		83	0.7		58.0	39.0	11.6
23 - 6	5.93	190			3.7	0.50	100		91	1.0		44.6	31.9	2.9
23 - 7	4.48	750			1.6	0.50	100		63	0.4		69.0	43.5	30.1
23 - 8	6.13	125			4.9	0.50	100		94	1.3		35.3	32.4	2.0

Sample	Sulfite Balance m.moles/l	Ca Inlet		Ca Exit		Calcium Balance	
		Total m.moles/l	Solution m.moles/l	Total m.moles/l	Solution m.moles/l	m.moles/l	m.moles/l
23 - 1	-30.3	50.5	8.3	21.0	8.3	-29.5	
23 - 2	-37.3	51.5	18.7	27.5	18.7	-24.0	
23 - 3	-5.9	49.7	6.0	40.0	6.0	-9.7	
23 - 4	-10.0	50.0	5.8	42.0	5.8	-6.0	
23 - 5	-19.0	45.0	9.8	38.8	9.8	-6.2	
23 - 6	-12.7	50.0	6.5	37.5	6.5	-12.5	
23 - 7	-25.5	50.0	22.6	38.0	22.6	-12.0	
23 - 8	-2.9	52.5	8.5	43.3	8.5	-9.2	
Average-18.0				Average -13.9			

Table XVII. Summary Results -- Scrubbing Liquid, 0.5% CaO₃ Slurry

Expt.	pH	SO ₂ out ppm	Make up gph	Stoich.	Recycle gpm	L/G	SO ₂ removed %	SO ₂ removed m.moles/l	Sulfite by Titration total m.moles/l	Sulfite balance m.moles/l	Ca inlet total m.moles/l
8-1	4.5	850	-2.7	.73	1.0	200	57	38.9	-	-	28
8-2	5.0	785	-2.75	.75	1.0	200	61	39.9	25.1	-14.8	51
8-3	5.1	500	-2.7	.73	1.0	200	75	50.9	28.2	-22.7	52
8-4	5.0	710	-2.9	.79	0.5	100	64	40.3	37.4	- 2.9	52
8-5	5.05	850	2.9	.79	0.25	50	57				
8-6	5.4	400	-2.9	.79	1.0	200	80	50.5	22.5	-28.0	53
8-7	6.4	165	7.2	1.95	1.0	200	92				
8-8	6.42	165	-5.2	1.4	1.0	200	92	32.2	26.0	-6.2 -14.9	52

Expt.	Ca Exit Total Solution m.moles/l	Calcium balance m.moles/l
8-1	30	33.2
8-2	39	30.8
8-3	39	25.1
8-4	46	17.5
8-6	46	6.6
8-8	50	7.4
Average - 6.3		

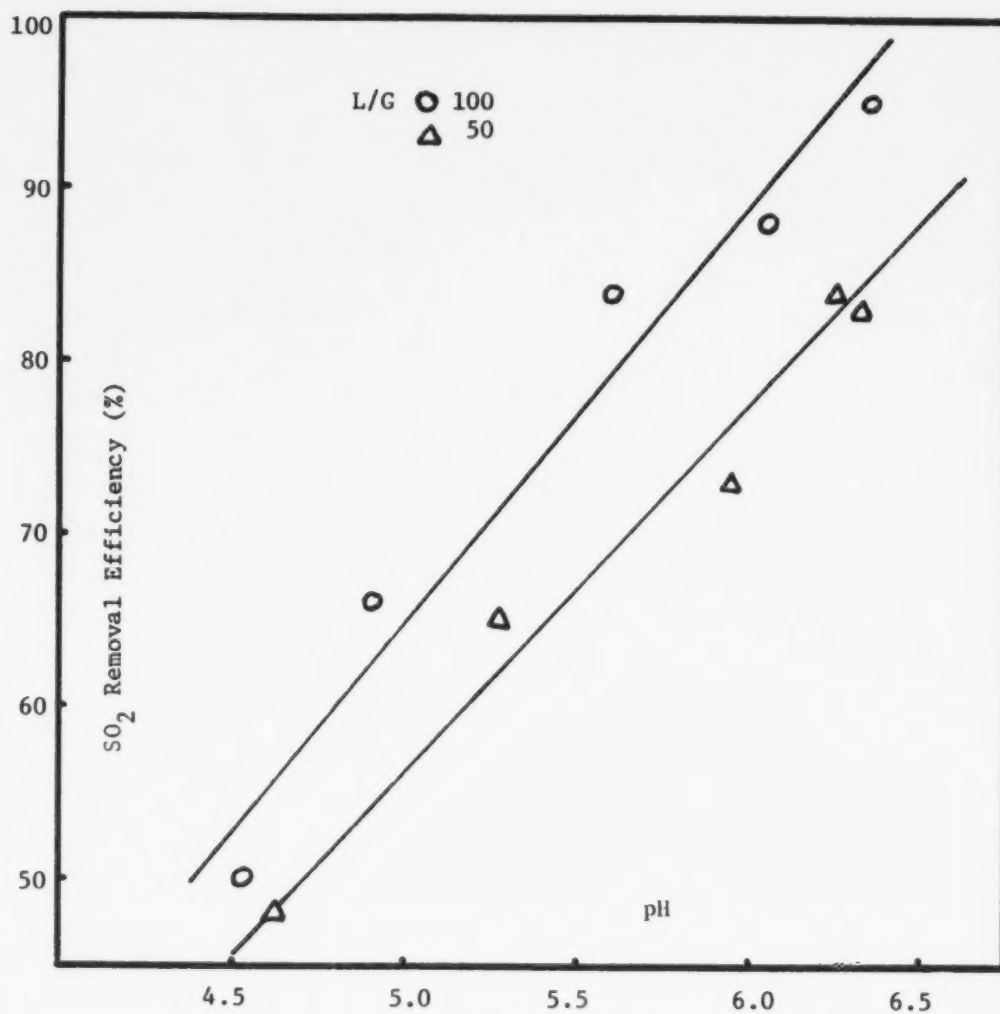


Figure 13. Sulfur Dioxide Removal Efficiency as a Function of pH—0.5% CaCO₃ (125° F., No Oxygen).

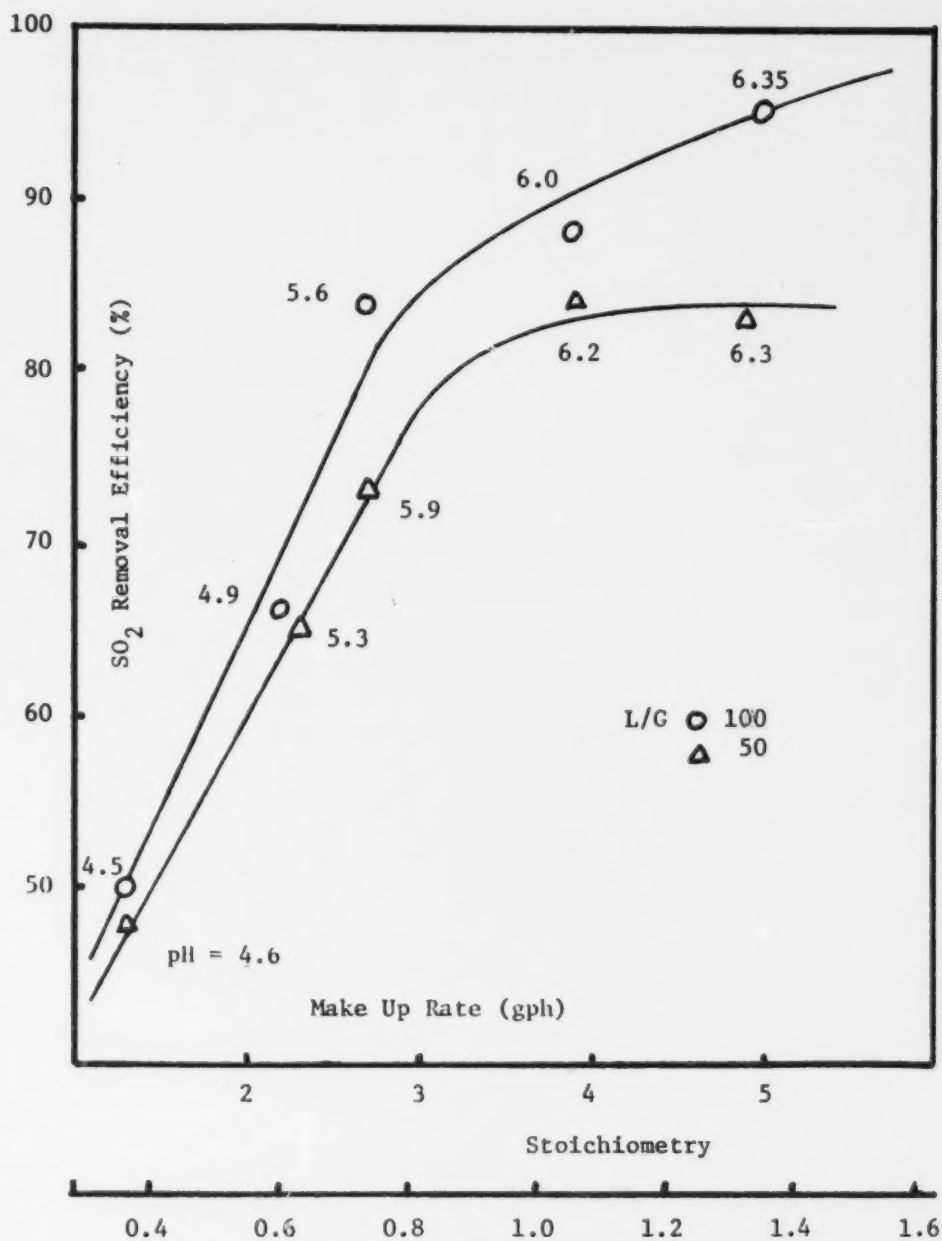


Figure 14. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate--0.5% CaCO₃ (125° F., No Oxygen).

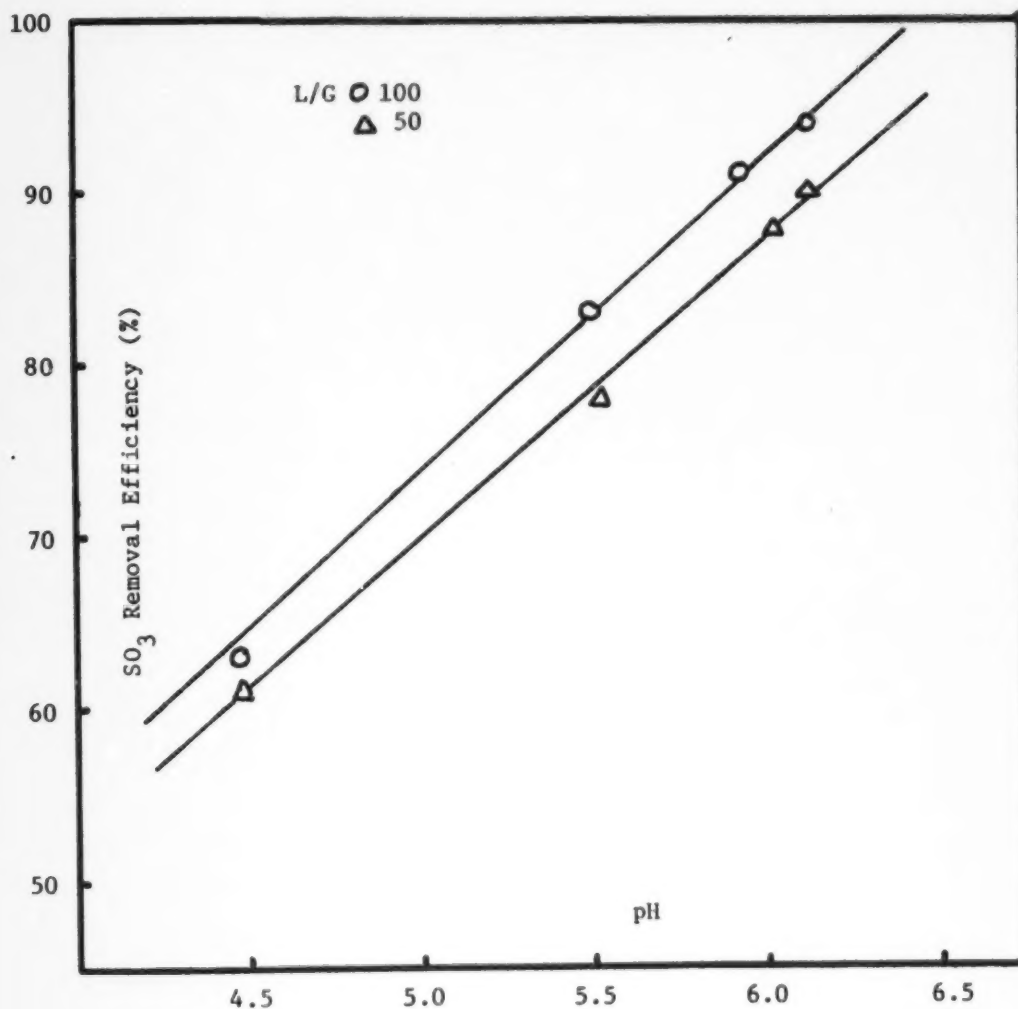


Figure 15. Sulfur Dioxide Removal Efficiency as a Function of pH--0.5% CaCO₃ (100° F., No Oxygen).

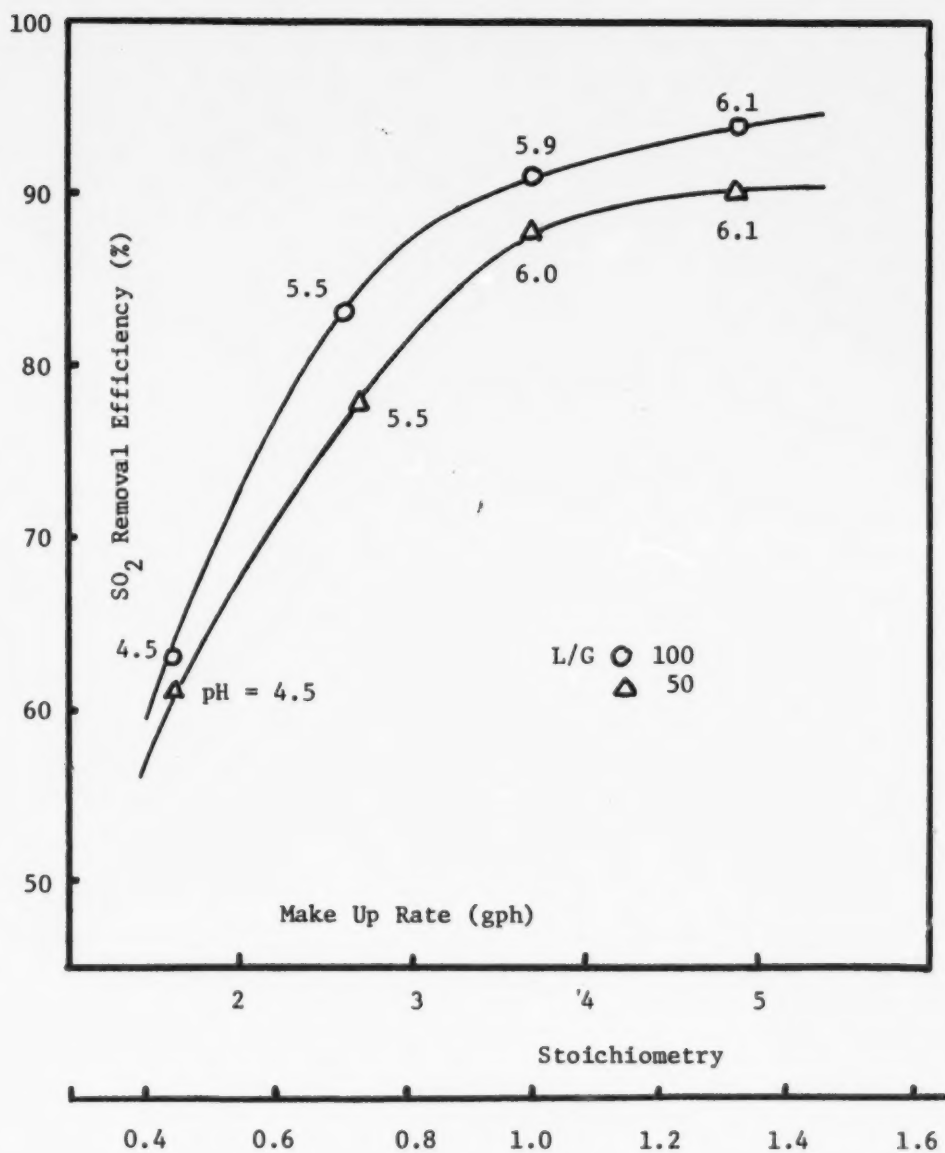


Figure 16. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate--0.5% CaCO₃ (100° F., No Oxygen).

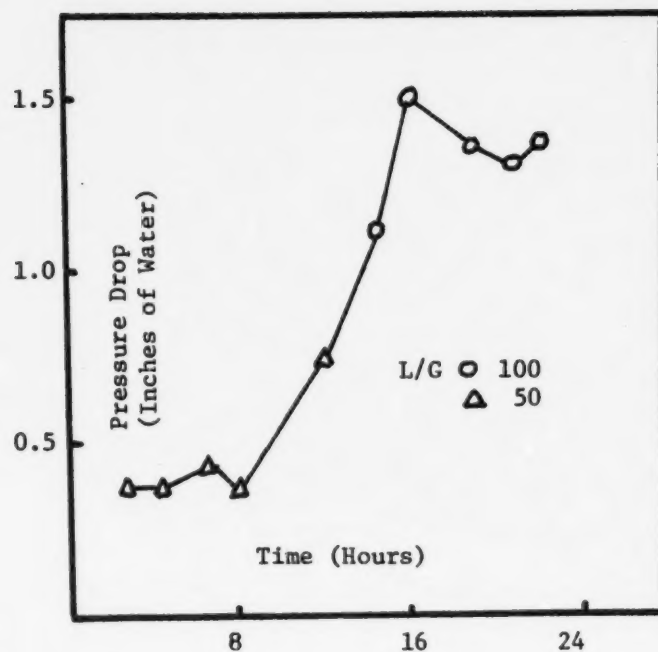


Figure 17. Pressure Drop as a Function of Operating Time--0.5% CaCO_3 (125° F., No Oxygen).

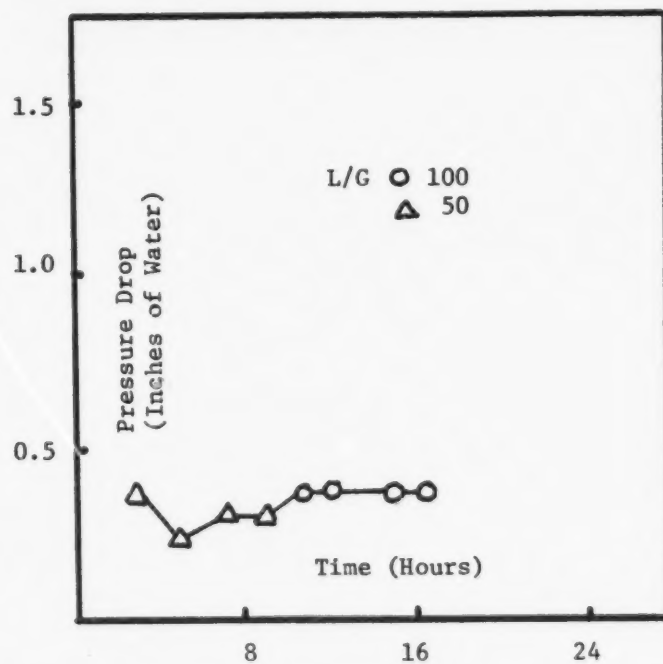


Figure 18. Pressure Drop as a Function of Operating Time--0.5% CaCO_3 (100° F., No Oxygen).

Table XVIII. Summary Results--Scrubbing Liquid, 1.0% CaCO₃

Initial pH 7.9		Gas Temp. 275 ^o F								
Inlet SO ₂ 2000 ppm		Liquid Temp. 125 ^o F								
N ₂ flow 5 scfm										
NO oxygen										
Sample	pH	SO ₂ Out ppm	Make Up Rate gph	Recycle gpm	L/G	SO ₂ Removal %	Stoich.	SO ₂ Removed m.moles/l	Sulfite by Titration	
								Total m.moles/l	Solution m.moles/l	
25 - 0			1.8					90.6	54.2	3.4
25 - 1	6.63	175	4.7	0.25	50	91	2.5	35.3	30.8	1.4
25 - 2	6.65	175	3.9	0.25	50	91	2.1	42.4	36.1	1.5
25 - 3	6.75	40	1.8	0.50	100	98	1.0	110.0	73.3	1.6
25 - 4	6.78	0	4.9	0.50	100	100	2.6	37.5	49.3	0.7
25 - 5	6.63	240	1.8	0.25	50	88	1.0	96.2	58.0	0.0
Sample	Sulfite Balance m.moles/l	Ca Inlet Total m.moles/l	Ca Exit		Calcium Balance					
			Total m.moles/l	Solution m.moles/l	Total m.moles/l					
25 - 0	-36.4	98.7	61.4	8.4	-37.3					
25 - 1	-4.5	99.0	93.5	6.0	-5.5					
25 - 2	-6.3	98.5	87.3	5.0	-11.2					
25 - 3	-36.7	97.3	108.0	4.4	+10.7					
25 - 4	+11.8	97.9	99.5	4.6	+1.6					
25 - 5	-38.2	98.5	76.7	4.8	-21.8					
Average-18.4						Average -10.6				

Table XIX. Summary Results -- Scrubbing Liquid, 1.0% CaCO₃

		Initial pH 8.4		Gas Temp. 275° F		Liquid Temp. 100° F			
		Inlet SO ₂ 2000 ppm		N ₂ flow 2 5 scfm					
		No Oxygen							
Sample	pH	SO ₂ Out ppm	Make Up Rate gph	Recycle gpm	L/C	SO ₂ Removal %	Stoich.	SO ₂ Removed m.moles/l	Sulfite by Titration Total Solution m.moles/l
24 - 1	6.60	175	2.6	0.25	50	91	1.4	61.7	35.9
24 - 2	6.53	215	1.7	0.25	50	89	0.9	92.3	49.3
24 - 3	6.63	125	5.2	0.25	50	94	2.8	33.1	33.1
24 - 4	6.68	150	3.5	0.25	50	93	1.9	48.5	35.6
24 - 5	6.70	60	2.6	0.50	100	97	1.4	66.5	53.8
24 - 6	6.78	40	3.5	0.50	100	98	1.9	50.9	55.4
24 - 7	6.55	40	1.7	0.50	100	98	0.9	107.0	65.8
		Sulfite Balance m.moles/l		Ca Inlet Total m.moles/l		Ca Exit Total Solution m.moles/l			
24 - 1		-25.8		98.3		65.5			
24 - 2		-43.0		98.3		69.1			
24 - 3		0.0		103.0		83.9			
24 - 4		-12.9		99.8		92.4			
24 - 5		-12.7		102.0		95.9			
24 - 6		+4.5		98.7		91.5			
24 - 7		-41.2		97.5		99.8			
Average		-18.7							
				Calcium Balance m.moles/l		Average -14.2			
						-32.8			
						-29.2			
						-19.1			
						-7.4			
						-6.1			
						-7.2			
						+2.3			

In Figure 19, sulfur dioxide removal efficiency for 1.0% calcium carbonate at 125°F is seen to vary linearly with pH, but much more rapidly than for 0.5% calcium carbonate (Figure 13). Furthermore, the L/G effect seen with the 0.5% slurry is not seen with the 1.0% slurry. In Figure 20, results for the 1% slurry are plotted as a function of stoichiometry. Removal rate is higher at L/G = 100 than at L/G = 50. However, in contrast to the 0.5% slurry (Figure 14), there is no fall-off in efficiency at low makeup rate. However, the makeup rate could not be reduced below a stoichiometry of 0.8 because of pump limitations. Results for the 1.0% slurry at 100°F are shown in Figures 21 and 22, and differ very little for the corresponding plots at 125°F (Figures 19 and 20). Thus, the temperature effects noted for the 0.5% slurry are not seen with the 1% slurry.

The efficiencies (88-100%) are somewhat higher than in the initial shake-down runs (Figure 8), probably due to higher pressure drop through the column. (See Figure 23.) Although the pressure drop increased consistently throughout runs XVIII and XIX, column operation was still satisfactory. After a total of 21 hours of operating time, scaling on the packing had become very severe causing abnormally high pressure drops at high liquid recycle rates.

0.6% Limestone Slurries

Scrubbing Efficiency and Scaling in the Absence of Oxygen

Experimental runs with 0.6% limestone slurries in the absence of oxygen in the flue gas are summarized in Tables XX-XXV. Results are plotted in Figures 24-28.

Figure 24 shows that at 125°F SO₂ removal efficiency varies linearly with the pH of the scrubbing solution over the range 4.5 to 6.0, in a similar manner to that observed with 0.5% CaCO₃ (cf., Figure 13).

Measurements of removal efficiency as a function of stoichiometry over the range 0.3 - 1.4 are plotted in Figure 25. Results are similar to those plotted in Figure 14 for 0.5% CaCO₃. With limestone, more than 90% of the SO₂ was removed down to a stoichiometry of 0.7 and a pH of 5.8. The efficiency then fell off rapidly down to 50% at a stoichiometry of 0.3.

For limestone, run at 125°F in the absence of oxygen, sulfite scale build-up is reflected in the pressure drop vs. time curve shown in Figure 26. During the first 8 to 10 hours on-line, the pressure drop across the column remained low; then there was a gradual increase in pressure drop due to the gradual build-up of sulfite scale on the column packing. The first minor shut-down came after about 26 hours on-line when it became difficult to maintain the recycle rate, due to scale formation in the recycle rotometer and neighboring lines. However, this did not cause complete blocking and was only a problem at constrictions in the recycle line. There was a steady build-up of sulfite scale on the column, however; and at the end of 52 hours, the pressure drop had

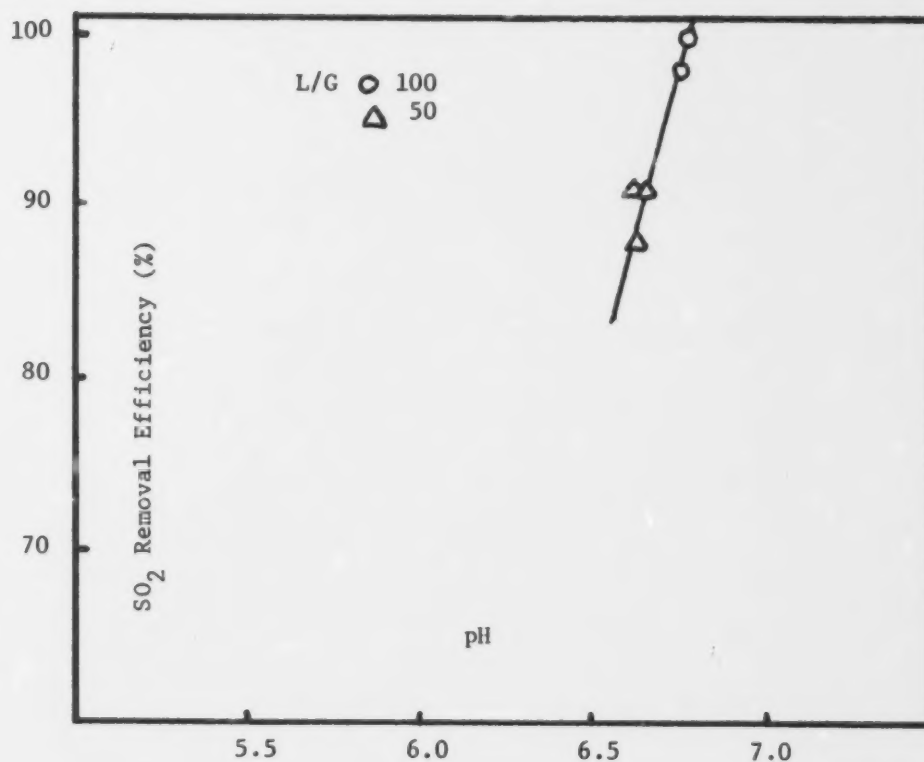


Figure 19. Sulfur Dioxide Removal Efficiency as a Function of pH--1.0% CaCO₃ (125° F., No Oxygen).

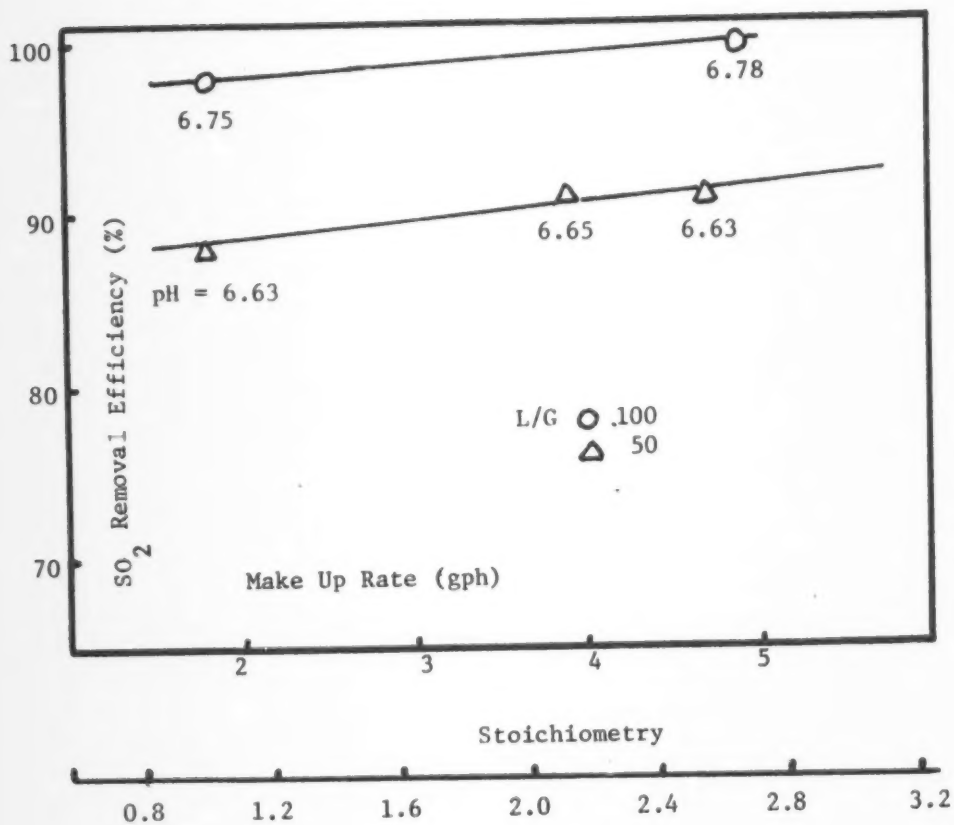


Figure 20. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate--1.0% CaCO₃ (125° F., No Oxygen)

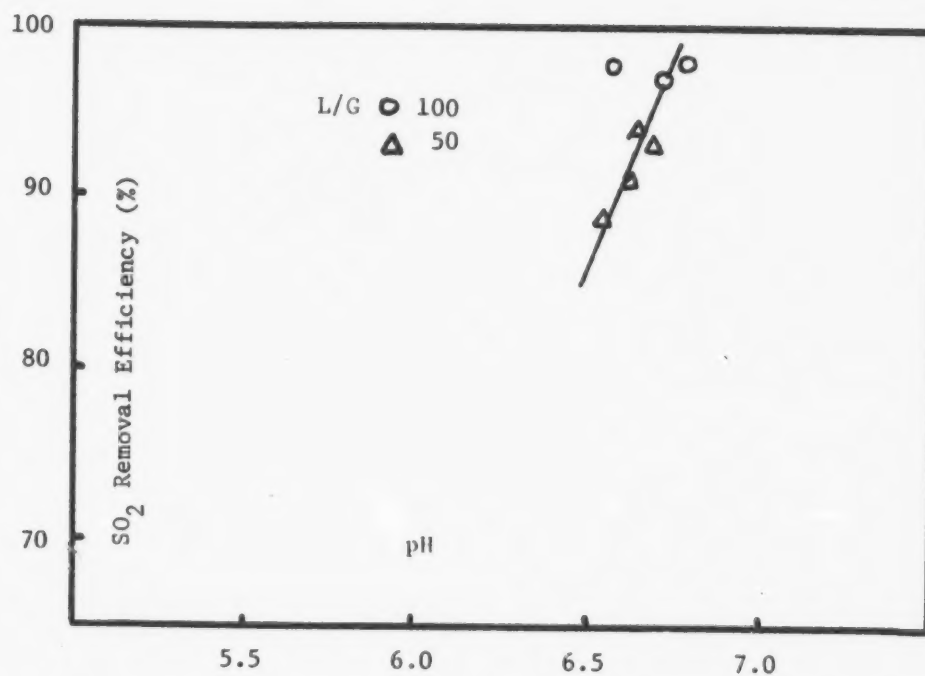


Figure 21. Sulfur Dioxide Removal Efficiency as a Function of pH--1.0% CaCO₃ (100° F., No Oxygen).

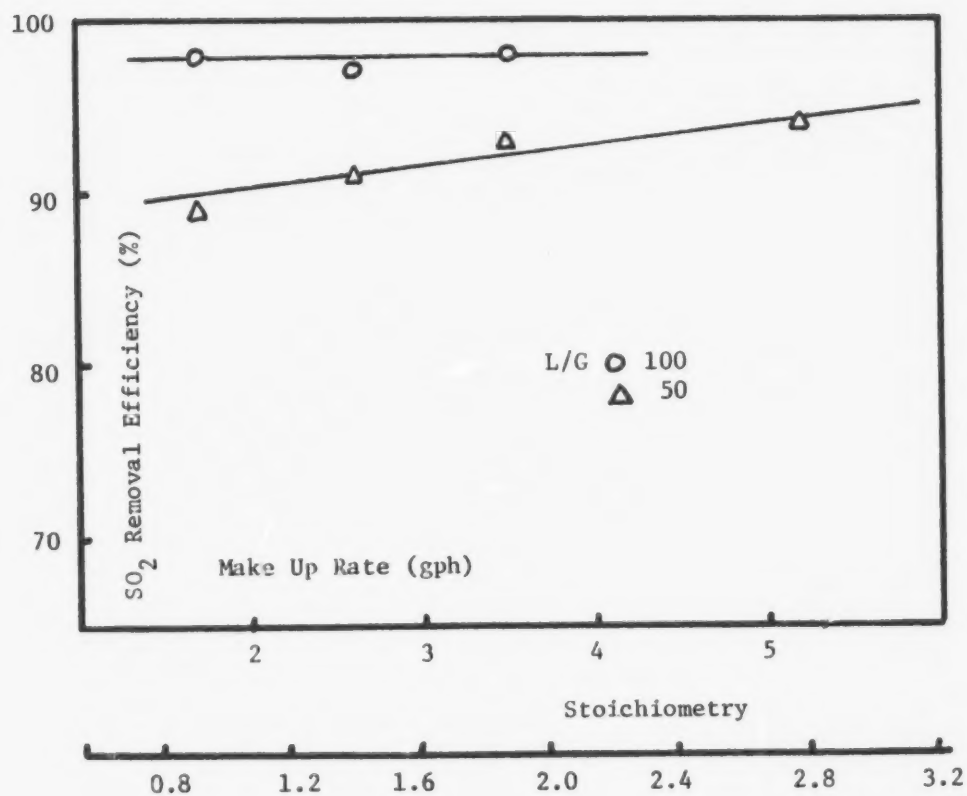


Figure 22. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate--1.0% CaCO₃ (100° F., No Oxygen)

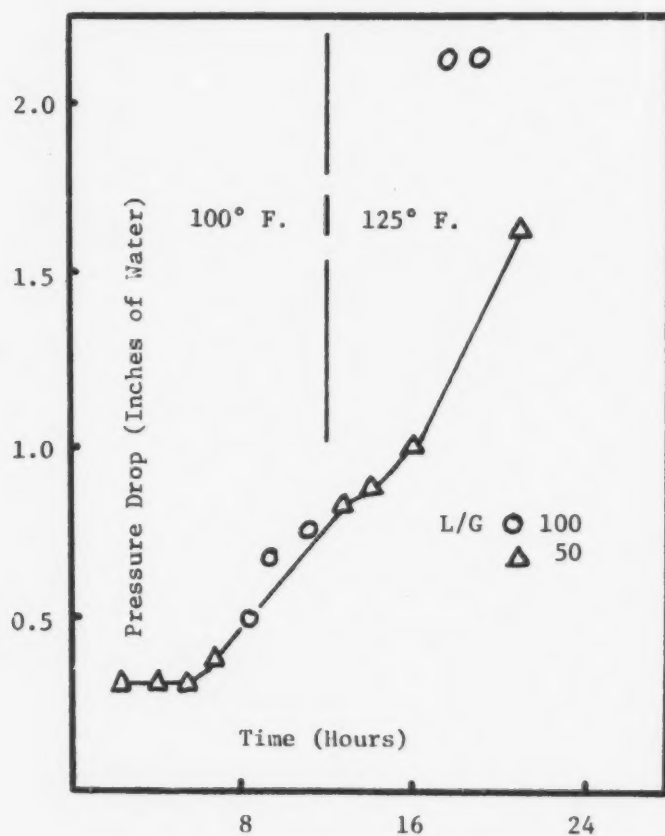


Figure 23. Pressure Drop as a Function of Operating Time--1.0% CaCO_3 (100° F. and 125° F., respectively, No Oxygen).

Table XX. Summary Results -- Scrubbing Liquid 0.6% Shawnee Limestone

Run 15

Gas temperature 275 ° F
Liquid Temperature 125 ° F

Initial pH 7.8
Inlet SO₂ 2300 ppm
N₂ flow 5 scfm
No oxygen

pH	SO ₂ out ppm	Make up rate gph	Recycle gpm	L/G	SO ₂ Removal %	Stoichiometry
6.08	63	5.1	0.5	100	97	1.2
5.90	125	3.9	0.5	100	93	1.0
5.80	235	2.8	0.5	100	90	.7
4.90	750	1.7	0.5	100	67	.4
4.5	995	1.7	0.5	100	57	.4
5.00	710	1.7	0.5	100	69	.4
4.43	1025	1.4	0.5	100	55	.3
4.40	1100	1.3	0.5	100	52	.3
4.38	1140	1.4	0.5	100	50	.3

Table XXI. Summary Results--Scrubbing Liquid, 0.5% Shawnee Limestone

Expt.	pH	SO ₂ out ppm	Make up gph	Stoich.	Recycle gpm	L/G	SO ₂ removed		SO ₂ removed m. moles/l	Sulfite by Titration		Sulfate	
							%	m. moles/l		Total m. moles/l	Solution m. moles/l	Soln	Solid
Inlet SO ₂ 2000 ppm Initial pH 6.8 N ₂ rate 5 scfm Lfg. Temp 100° F Gas Temp 255° F O ₂ rate 12 scfh (4%)													
12 - 1	5.43	350	5.3	1.4	0.5	100	82.5	33.5	12.4	6.6		11.7	1.2
12 - 2	4.8	950	2.9	0.8	0.5	100	52.5	36.2	22.2	22.8			
12 - 3	4.55	1025	2.9	0.8	0.25	50	49	36.0	21.0	22.0		17.1	0
12 - 4	5.4	330	5.4	1.46	0.25	50	83.5	32.8	14.2	5.0			
12 - 5	5.8	150	5.4	1.46	0.5	100	92.5	36.6	23.5	0		0.7	0

Expt.	Sulfur Balance m. moles/l	Ca Inlet total m. moles/l	Ca Exit		Calcium balance m. moles/l
			Total m. moles/l	Solution m. moles/l	
12 - 1	- 6.2	43.5	18.0	8.8	-25.5
12 - 2		43.0	20.5	20.3	-22.5
12 - 3	+ 2.1	44.5	21.0	21.3	-23.5
12 - 4		44.5	24.5	11.6	-20.0
12 - 5	-12.1	44.0	42.5	9.2	-1.5
Average	-6.1				Average -18.6

Table XVII. Summary Results--Scrubbing Liquid, 0.5% Shawnee Limestone

Expt.	pH	SO ₂ out ppm	Make up gph	Stoich.	Recycle gpm	L/G	SO ₂ removed		SO ₂ removed		Sulfite by Titration		Sulfate	
							%	m.moles/l	%	m.moles/l	Total m.moles/l	Solution m.moles/l	Soln	Solid
13 - 1	5.5	260	5.4	1.46	0.5	100	87	34.5		17.5	3.2	11.9	11.9	2.4
13 - 2	5.1	600	2.9	0.8	0.5	100	70	53.0		70.2	11.6	18.0	18.0	0.9
13 - 3	5.1	750	2.9	0.8	0.25	50	62.5	46.7		9.5	9.4	18.9	18.9	1.2
13 - 4	5.3	520	5.4	1.46	0.25	50	74							

Expt.	Sulfur		Ca Inlet		Ca Exit		Calcium	
	balance		total		Total Solution		balance	
	m. moles/l		m. moles/l		m. moles/l		m. moles/l	
13 - 1	- 2.7		44.5		30.5	16.8	-14.0	
13 - 2	-13.9		46.5		25.5	10.6	-21.0	
13 - 3	-17.1		47.0		27.5	22.6	-19.5	
Average	-11.2						Average	-16.1

Table XXIII. Summary Results--Scrubbing Liquid, 0.6% Shawnee Limestone

Expt.	pH	SO ₂ out ppm	Inlet SO ₂ , 2000 ppm Initial pH 8.1 N ₂ rate 5 scfm		Recycle gph	L/G	SO ₂ removed %	SO ₂ Removed m.moles/l	Sulfite by Titration		Ca Inlet Total m.moles/l
			Make up gph	Stoich.					Total m.moles/l	Solution m.moles/l	
14 - 1	5.93	390	5.3	1.7	0.5	100	81	32.1	12.0	0	50.0
14 - 2	5.45	606	2.9	0.95	0.5	100	70	51.3	21.0	7.6	48.5
14 - 3	5.3	775	2.9	0.95	0.75	50	63.5	46.0	17.7	9.4	49.5
14 - 4	5.6	520	5.3	1.7	0.25	50	74	39.1	13.5	0	55.0
14 - 5	5.9	280	5.3	1.7	0.5	100	86	100	14.2	0	60.0
14 - 6	5.9	310	5.3	1.7	0.5	100	84.5	34.0	26.5	1.6	56.0
14 - 7	5.6	520	2.9	0.95	0.5	100	74	53.5	71.5	5.8	56.0
14 - 8	5.4	745	2.9	0.95	0.25	50	63	43.7	15.0	0	52.5
14 - 9	5.7	540	5.2	1.7	0.25	50	73	29.8	22.8	0	58.5
14 - 10	6.1	260	5.2	1.7	0.5	100	87	35.8			

Expt.	Ca Exit Solution		Calcium Balance	
	Total m.moles/l		m.moles/l	
14 - 1	28.0	9.8	-22.0	
14 - 2	24.5	11.9	-24.0	
14 - 3	31.5	22.7	-16.0	
14 - 4	31.0	16.6	-24.0	
14 - 6	39.5	11.4	-20.5	
14 - 7	42.5	10.0	-13.5	
14 - 8	34.5	14.4	-21.5	
14 - 9	34.5	13.4	-18.0	
14 - 10	54.5	8.4	-4.0	
			Average -18.4	

Table XXIV. Summary Results--Scrubbing Liquid, 0.6% Shawnee Limestone

Expt.	N ₂ flow scfm	pH	SO ₂ out ppm	SO ₂ inlet ppm	Initial pH 8.5 Inlet SO ₂ 2300 ppm No Oxygen	Gas Temperature 275° F Liquid temperature 125° F	Recycle gpm	L/G	SO ₂ Removal %	Stoich.	SO ₂ removed m.moles/l	Sulfite by Titration		Sulfite Balance m.moles/l
												Total m.moles/l	Solution m.moles/l	
15-1	5	5.75	540	690	4.8	0.5	100	77	1.1	33.6	16.0	3.8		-17.6
15-2	5	5.50	690	690	2.9	0.5	100	70	.7	51.0	15.2	7.6		-35.8
15-3	5	5.20	640	640	3.9	0.5	100	73	1.0	39.6	21.2	8.0		-18.4
15-4	5	5.60	705	705	3.9	0.25	50	69	1.0	36.9	16.0	5.2		-20.9
15-5	5	5.35	795	795	7.8	0.25	50	66	.7	48.7	18.2	7.6		-30.5
15-6	5	5.80	500	500	4.7	0.25	50	79	1.1	34.8	16.7	0		-18.1
15-7	5	6.03	280	280	4.8	0.5	100	88	1.1	38.3	20.5	.4		-17.8
15-8	7	4.3	690	690	2.8	1.0	144	70	.5	74.3	57.2	20.8		-17.1
15-9	3	6.30	0	0	2.8	1.0	330	100	1.1	45.2	31.7	0		-13.5
15-10	5	5.55	260	260	2.7	1.0	700	89	.6	68.7	43.7	3.2	Average	-25.0
														-21.5

Expt.	Ca Inlet total m.moles/l	Ca Exit		Calcium Balance m.moles/l
		Total m.moles/l	Solution m.moles/l	
15-1	55.5	25.5	7.4	-30.0
15-2	55.0	16.4	9.2	-38.6
15-3	51.0	30.2	16.0	-20.8
15-4	55.0	19.7	9.8	-35.3
15-5	52.5	25.5	15.6	-27.0
15-6	61.5	29.0	8.8	-31.5
15-7	57.0	37.0	6.2	-20.0
15-8	56.0	51.0	35.0	-5.0
15-9	54.0	55.0	7.0	1.0
15-10	50.5	50.5	6.4	-5.0
				Average -21.2

Table XXV. Summary Results --Scrubbing Liquid, 0.6% Shawnee Limestone

Run 14

Initial pH 8.2			Gas temperature 2-5° F		Stoichiometry
Inlet SO ₂ 2300 ppm			Liquid Temperature 125° F		
pH	N ₂ flow 5 scfm		SO ₂ Removal %	L/G	
	O ₂ flow 12 scfh				
SO ₂ out ppm	Make up rate gph	Recycle gpm			
5.88	170	5.2	93	100	1.2
5.65	300	3.9	87	100	1.0
5.33	450	2.8	81	100	.7

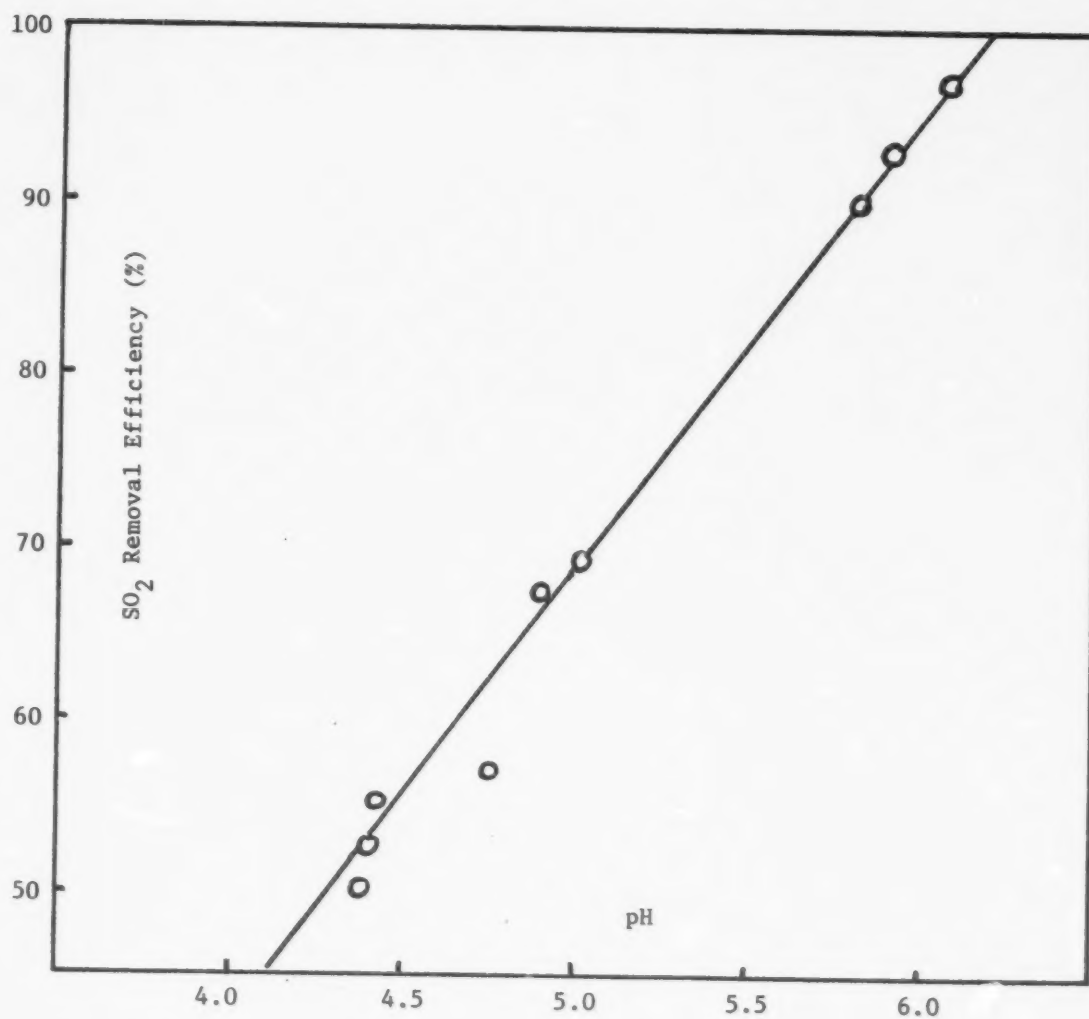


Figure 24. Sulfur Dioxide Removal Efficiency as a Function of pH--0.6% Shawnee Limestone (125° F., L/G = 100, No Oxygen)

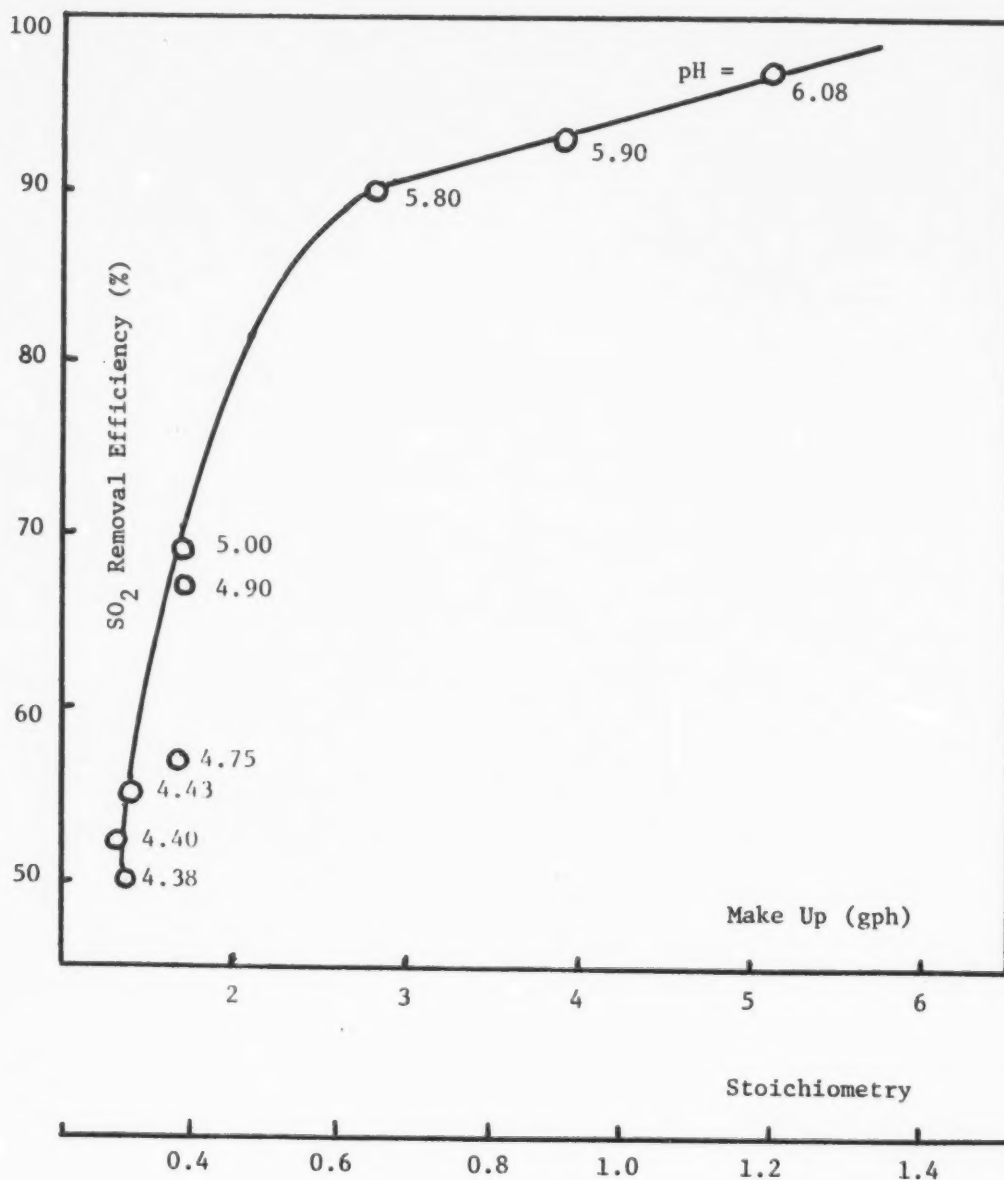


Figure 25. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate (Stoichiometry)--0.6% Shawnee Limestone (125° F., L/G = 100, No Oxygen)

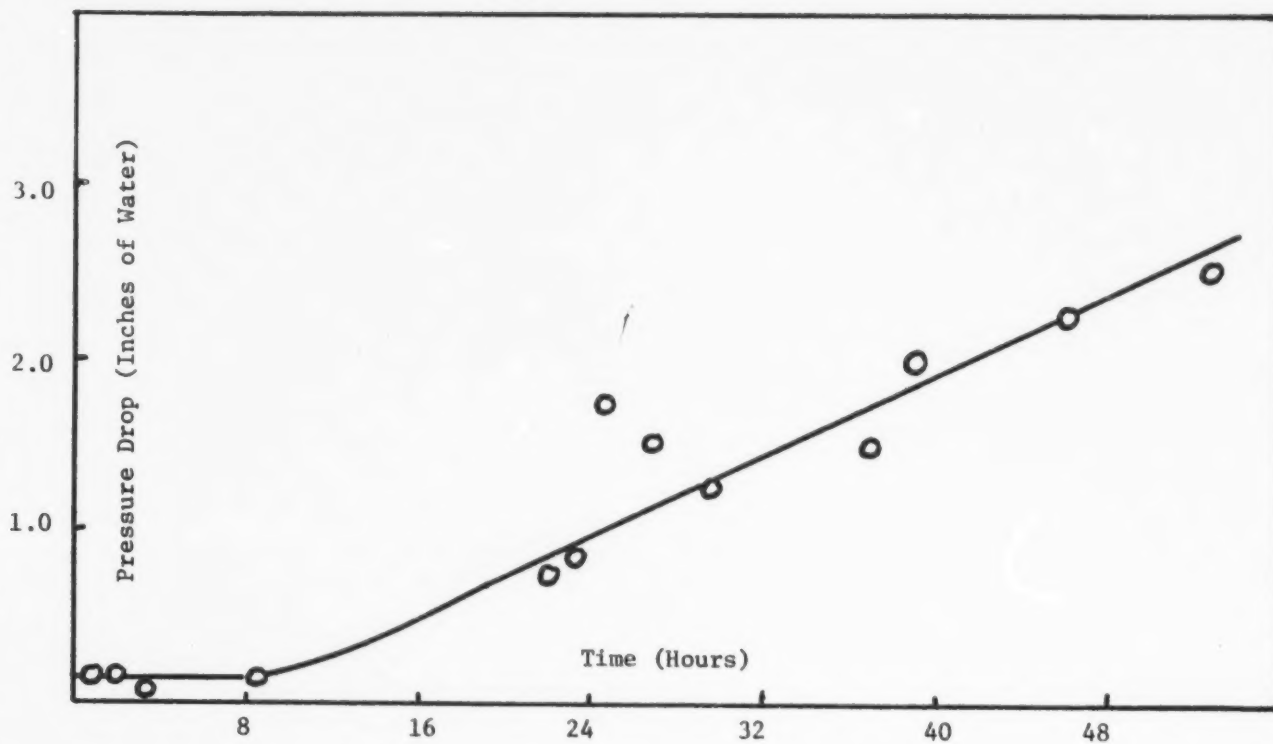


Figure 26. Pressure Drop as a Function of Operating Time
0.6% Shawnee Limestone (125° F., L/G = 100,
No Oxygen)

risen to 2.5 in. from an initial value of less than 0.25 in. The distributor at the top of the column became clogged with solids and was essentially inoperable. Some local flooding of the packed column was also observed, and the run was terminated.

During the extended runs to characterize sulfite build-up in limestone scrubbing, it was noted that the removal efficiency appeared to be increasing as the pressure drop across the column increased. Figure 27 shows that this appears to be a linear change and is about 20% for a pressure drop increase of 1.5 in. This increase in efficiency is probably due to an increased liquid residence time in the column. Although the high pressure drop was not obtained in the earlier experiments, changes in pressure drop could account for some of the variations in experimental data.

Scrubbing Efficiency and Scaling in the Presence of 4% Oxygen

Scaling and plugging due to sulfate was observed on two occasions during the runs with Shawnee limestone. In the first set of experiments, carried out at 100°F (Table XXII) and then 125°F (Table XXIII), the unit became inoperable after 17 hours on-line with plugging at the bottom of the hold tank, in the recycle pump and the recycle line to the scrubbing column. The second series of experiments (Table XXIII) were carried out at 125°F. In this instance, the plugging occurred after 12 hours on-line at a point between the hold tank and the makeup tank but not significantly in any other part of the apparatus. For both sets of experiments, there was no noticeable plugging of the packed column or change in pressure drop during operation. Deposits of scale were observed on the walls of the hold tank, and some of this deposit appeared to have detached itself from the walls and been carried down into the line to the makeup tank assisting in the plugging of this line.

Figure 28 plots removal efficiency against pH for two consecutive runs which were carried out to establish at what stage scaling or plugging would occur. It can be seen that there is little or no effect of sulfate build-up on the removal efficiency at a given makeup rate. (The repeat run is shown as solid circles and triangles.) Sulfate build-up did not apparently affect the removal efficiency up to the point where plugging occurred and the unit had to be shut down.

Scaling problems in the presence of oxygen were quite different from those reported previously when oxygen was excluded from the system. In the former case, plugging caused a complete shut-down after about 12 hours at 125°F. However, without oxygen, at the same temperature, the run was continued for a period of about 52 hours with only one minor shut-down to remove some scale in the recycle line.

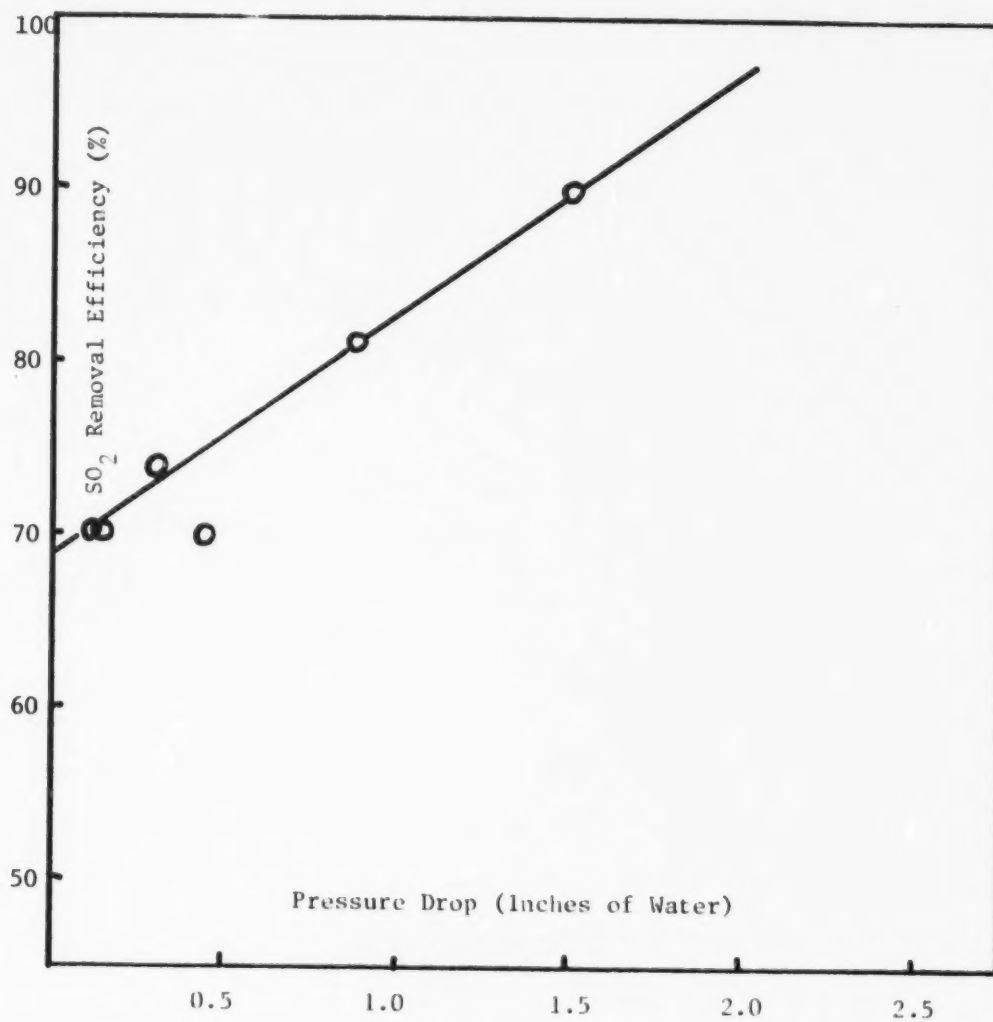


Figure 27. Sulfur Dioxide Removal Efficiency As A Function of Pressure Drop - 0.6% Shawnee Limestone (125°F, L/G = 100, Make Up Rate = 2.9 gph)

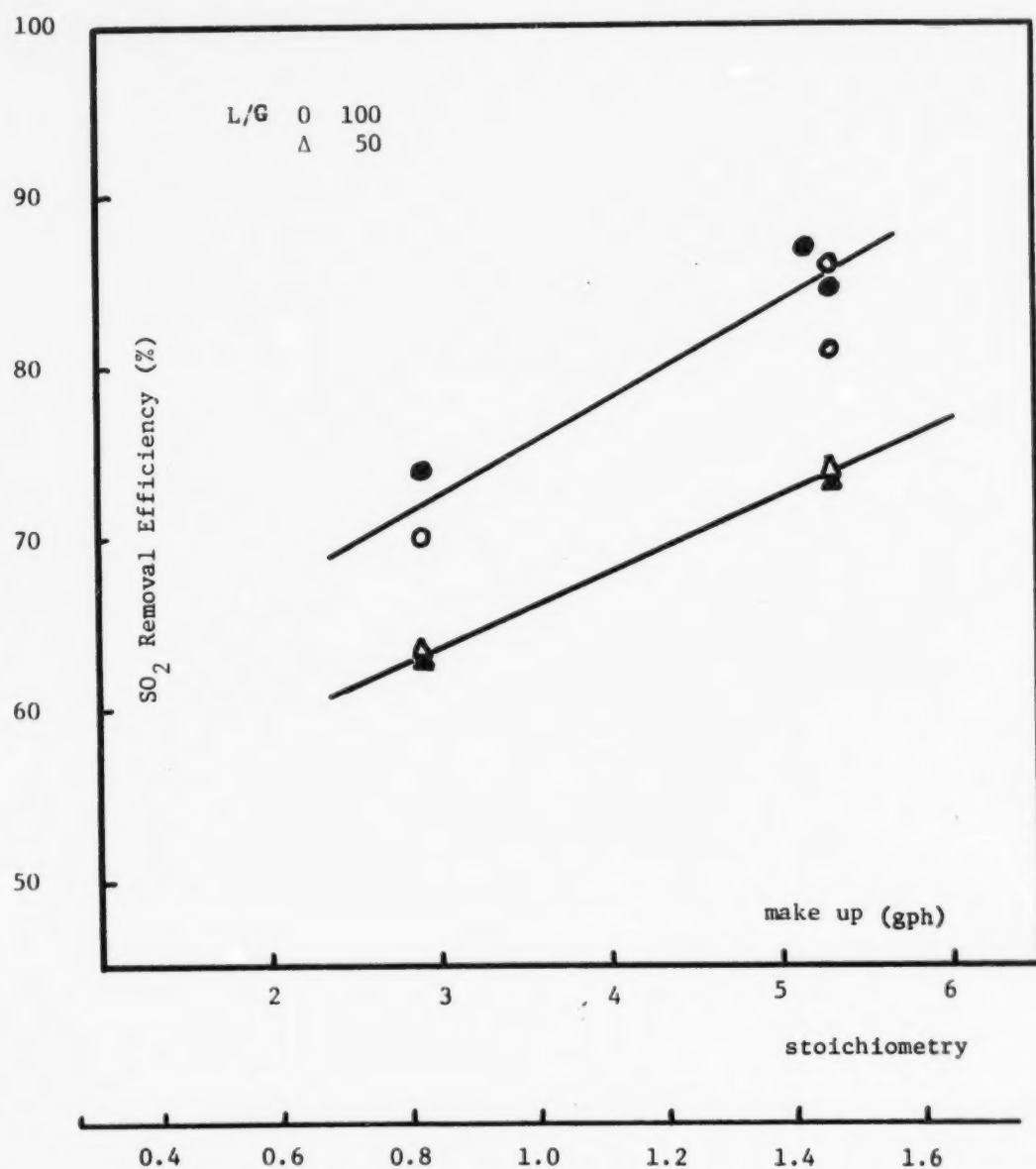


Figure 28. Sulfur Dioxide Removal for Shawnee Limestone. Consecutive Runs in Presence of 4% Oxygen. (○, Δ first run; ●, ▲ second run.)

0.5% CaSO₃ Slurries

In order to separate out the roles of calcium sulfite and calcium carbonate in the SO₂ removal process, a series of experiments were carried out using a 0.5% CaSO₃ slurry as the scrubbing medium. Results are given in Tables XXVI-XXIX and in Figures 29-37.

Scrubbing Efficiency in the Absence of Oxygen

SO₂ removal rates for calcium sulfite slurries are considerably lower than those obtained with carbonate slurries under the same process operating conditions. Data from run XXVI is plotted as a function of pH in Figure 29 for a temperature of 125°F. The same data are plotted as a function of makeup rate in Figure 3C. For calcium sulfite solutions, the concept of stoichiometry is not applicable, because the chemical equilibrium limits the reaction before the solid sulfite present has all been utilized. In Figure 30, there is a small effect of L/G ratio (or liquid rate) on the SO₂ removal efficiency at very high makeup rates; but the curves converge to a common value at low makeup rates.

Scrubbing Efficiency in the Presence of 4% Oxygen

The presence of oxygen at 125°F (comparing Figures 29 and 31) does not effect the results as a function of pH; and, although there is some scatter in the data points, there appears to be no effect of different L/G ratios within experimental error. A small increase in removal efficiency with L/G is seen when the data are plotted as a function of makeup rate in Figure 32; but the curves for L/G = 100, and L/G = 50 appear to converge at low makeup rate, similar to the results in the absence of oxygen (c.f., Figure 30).

At 100°F, data from run XXVIII do show a small effect of L/G with higher removal efficiencies for L/G = 50 at 100°F are only very slightly higher than the SO₂ removal efficiencies obtain in run XXVI at 125°F (c.f., Figures 29 and 33). In Figure 34, the 100°F data are plotted as a function of makeup rate. Removal efficiency is somewhat higher than at 125°F (c.f., Figure 32); and a small L/G effect is again noted.

Scrubbing Efficiency in the Presence of 4% Oxygen and 13% Carbon Dioxide

In run XXIX (Figure 35) 13% carbon dioxide was added to the gas stream, and the data as a function of pH appeared to be identical with run XXVI where CO₂ was absent. In Figure 36, the data are shown as a function of makeup rate. At L/G = 50, the removal efficiencies are similar to those obtained in the absence of CO₂. At L/G = 100, the increase in removal efficiency in the presence of CO₂ appears to be somewhat greater than when CO₂ is excluded.

Table XXVI. Summary Results--Scrubbing Liquid 0.5% CaSO₃

Sample	pH	SO ₂ Out ppm	Make up Rate gph	N ₂ flow 2 5 scfm	Recycle gpm	L/G	SO ₂ Removal %	Sulfite* Input m.moles/l	Sulfite by Titration		Sulfite Balance m.moles/l
									Total m.moles/l	Solution m.moles/l	
18-1	4.15	1125	5.2	Initial pH 4.8 Inlet SO ₂ 2300 ppm Gas temperature 275° F Liquid temperature 125° F	1.0	200	51	59	44.75	32.2	-14.2
18-2	4.2	1175	5.2		.50	100	49	59.1	41.1	28.2	-18.0
18-3	4.2	1250	5.2		.25	50	46	58.3	39.5	30.8	-18.8
18-4	4.1	1450	2.8		.25	50	37	68.2	44.1	36.8	-24.1
18-5	4.0	1475	2.9		.50	100	36	65.6	49.1	39.4	-16.5
18-6	3.95	1475	2.8		1.0	200	36	65.9	54.2	40.6	-11.7
18-7	3.93	1600	1.7		.50	100	30	75.3	39.2	40.6	-36.1
18-8	3.9	1675	1.7		.25	50	27	72.0	44.5	45.0	-27.5
18-9	4.35	1325	3.9		.25	50	43	62.2	35.7	32.0	-26.5
18-10	4.25	1325	3.9		.50	100	43	61.8	45.2	37.6	-16.6
18-11	4.18	1300	3.9		1.0	200	44	62.6	53.1	41.4	-9.5
18-12	4.3	1040	6.8		1.0	200	55	57.1	50.5	33.6	-6.6
18-13	4.4	1075	6.8		.50	100	53	53.4	41.3	29.8	-12.1
18-14	4.45	1125	6.8		.25	50	51	52.2	41.8	29.2	-10.4
18-15	4.0	1625	1.7		1.0	200	29	75.1	61.0	51.4	-14.1
18-16	4.1	1400	2.7		1.0	200	39	68.5	58.8	46.2	-9.7
											Average -17.1

*Sulfite Input = SO₂ Removed - Sulfite in Feed.

Sample	Ca Inlet		Ca Exit		Calcium	
	Total m.moles/l		Total m.moles/l	Solution m.moles/l	Total m.moles/l	Balance m.moles/l
18-1	38.5		37.0	24.6	-1.5	
18-2	39.0		40.5	27.3	+1.5	
18-3	39.5		36.5	25.6	-3.0	
18-4	41.0		37.0	28.9	-4.0	
18-5	39.5		40.2	29.2	+0.7	
18-6	39.5		44.7	31.1	+5.2	
18-7	39.0		36.0	32.8	-3.0	
18-8	39.0		35.7	34.8	-3.3	
18-9	39.0		33.2	29.1	-5.8	
18-10	38.5		36.7	30.4	-1.8	
18-11	39.0		44.5	32.4	+5.5	
18-12	40.0		41.7	24.8	+1.7	
18-13	37.0		33.0	22.2	-4.0	
18-14	36.5		33.7	21.6	-2.8	
18-15	39.0		45.2	34.8	+6.2	
18-16	39.0		44.5	31.7	+5.5	
					Average	-0.2

Table XXVII. Summary Results--Scrubbing Liquid, 0.5% CaSO₃

Initial pH 4.5 Inlet SO ₂ 2300 ppm N ₂ flow 2 5 scfm O ₂ flow 12 scfh									
Gas temperature 275° F Liquid temperature 125° F									
Sample	pH	SO ₂ Out ppm	Make Up Rate gph	Recycle gpm	L/G	SO ₂ Removal %	Sulfite* Input m.moles/l	Sulfite by Titration Total m.moles/l	Sulfite Balance m.moles/l
19 - 1	4.08	1350	3.9	0.5	50	41	60.6	42.0	-18.6
19 - 2	4.0	1465	2.8	0.5	50	36	64.2	40.2	-24.0
19 - 3	4.2	1200	6.9	0.5	50	48	52.6	42.0	-10.6
19 - 4	4.05	1650	1.7	0.5	50	28			
19 - 5	4.03	1500	2.8	1.0	100	35			
19 - 6	4.18	1300	3.9	1.0	100	44	61.9	46.7	-15.2
19 - 7	4.0	1625	1.7	1.0	100	30	76.4	50.5	-25.9
19 - 8	4.43	1075	6.7	1.0	100	53	54.7	49.0	-5.7
19 - 9	4.40	1200	5.2	1.0	100	48	57.0	43.2	-13.8
19 - 10	4.43	1300	5.2	0.5	50	44	56.7	34.3	-22.4
Gravimetric Determination of SO ₂									
		Ca Inlet Total m.moles/l	Ca Exit Total m.moles/l	Calcium Balance m.moles/l		Total m.moles/l	Solution m.moles/l		
Sample									
19 - 1		38.5	39.0		+0.5	26.7	15.5		
19 - 2		37.5	34.5		-3.0	22.1	18.0		
19 - 3		38.0	35.0		-3.0	19.0	19.8		
19 - 6		38.5	39.0		+0.5	27.4	16.8		
19 - 7		39.0	43.0		+4.0	36.1	17.8		
19 - 8		38.0	45.0		+7.0	37.0	18.4		
19 - 9		37.5	35.0		-2.5	25.2	24.6		
19 - 10		39.0	33.5		-5.5	23.0	19.5		
Average						27.1	18.6	Average	

*Sulfite Input = SO₂ Removed - Sulfite in Feed

Table XXVIII. Summary Results--Scrubbing Liquid, 0.5% CaSO₃

Sample	pH	Initial pH 4.93		Gas temperature 275° F		SO ₂ Out ppm	Make Up Rate gph	Recycle gpm	L/G	SO ₂ Removal %	Sulfite* Input m.moles/l	Sulfite by Titration		Sulfite Balance m.moles/l
		Inlet SO ₂ N ₂ flow O ₂ flow	2300 ppm 5 scfm 12 scfh	Total m.moles/l	Solution m.moles/l									
20 - 1	4.1	1415	2.7	0.5	50	39	70.2	46.7	43.8	-23.5				
20 - 2	3.93	1625	1.7	0.5	50	29	78.5	55.5	55.0	-23.0				
20 - 3	4.2	1225	5.0	0.5	50	47	58.0	49.0	40.2	-9.0				
20 - 4	3.83	1575	1.6	1.0	100	32	83.0	58.3	57.6	-24.7				
20 - 5	4.13	1175	5.0	1.0	100	49	58.1	52.5	42.8	-5.6				
20 - 6	3.98	1400	2.7	1.0	100	39	66.5	60.8	56.0	-5.7				
20 - 7	4.3	1075	6.8	0.5	50	53	57.5	44.5	36.2	-9.0				
20 - 8	4.25	965	6.8	1.0	100	58	53.8	49.3	39.4	-4.5				
													Average	-13.1

Determination of SO₂ =

Sample	Ca Inlet		Ca Extr		Calcium Balance m.moles/l	Gravimetric		Determination m.moles/l
	Total m.moles/l	Solution m.moles/l	Total m.moles/l	Solution m.moles/l				
20 - 1	39.5	38.0	35.5	-1.5	26.0	17.0		
20 - 2	41.0	39.0	40.0	-2.0	21.5	17.9		
20 - 3	38.0	37.0	39.3	-1.0	18.7	22.6		
20 - 4	40.0	40.0	40.3	0	21.5	18.0		
20 - 5	37.5	37.0	32.0	-0.5	18.2	20.7		
20 - 6	35.5	43.5	39.5	+8.0	21.6	19.4		
20 - 7	37.0	33.5	76.0	-3.5	17.5	18.6		
20 - 8	35.5	36.0	25.5	+0.5	24.8	17.6		
			Average	0.0	Average*	18.9		

*Sulfite Input = SO₂ Removed - Sulfite in Feed

Table XLIX. Summary Results--Scrubbing Liquid, 0.5% CaSO₃

Sample	pH	SO ₂ out ppm	Make Up Rate gph	Recycle gpm	L/C	SO ₂ Removal %	Sulfite*		Sulfite by Titration		Sulfite Balance m.moles/l
							Input m.moles/l	Total m.moles/l	Solution m.moles/l		
21 - 1	4.28	965	6.5	0.5	100	58	58.2	49.8	40.0	- 8.4	
21 - 2	3.98	1515	1.7	0.5	100	34	82.4	60.8	60.0	-21.6	
21 - 3	4.1	1075	4.8	0.5	100	53	58.7	57.2	46.8	- 1.5	
21 - 4	4.0	1300	2.7	0.5	100	44	72.3	58.5	55.8	-13.8	
21 - 5	4.2	1175	5.1	0.25	50	49	57.0	49.8	43.2	- 7.2	
21 - 6	3.93	1575	1.7	0.25	50	31	76.9	60.0	59.4	-16.9	
21 - 7	4.3	1100	6.1	0.25	50	52	53.5	43.6	37.6	- 9.9	
21 - 8	4.05	1475	2.7	0.25	50	36	66.3	53.8	40.3	-12.5	
									Average	-11.5	

Sample	Ca Inlet		Ca Exit		Calcium	
	Total m.moles/l	Solution m.moles/l	Total m.moles/l	Solution m.moles/l	Balance m.moles/l	
21 - 1	39.2	37.5	27.5	38.8	-1.7	
21 - 2	40.7	44.0	33.5	38.1	+8.5	
21 - 3	35.5	38.0	40.5	38.3	+2.5	
21 - 4	37.0	35.0	41.6	25.0	+2.2	
21 - 5	38.6	31.8	25.0	33.5	-3.7	
21 - 6	35.5	36.0			-2.6	
21 - 7	38.6				Average	-0.1

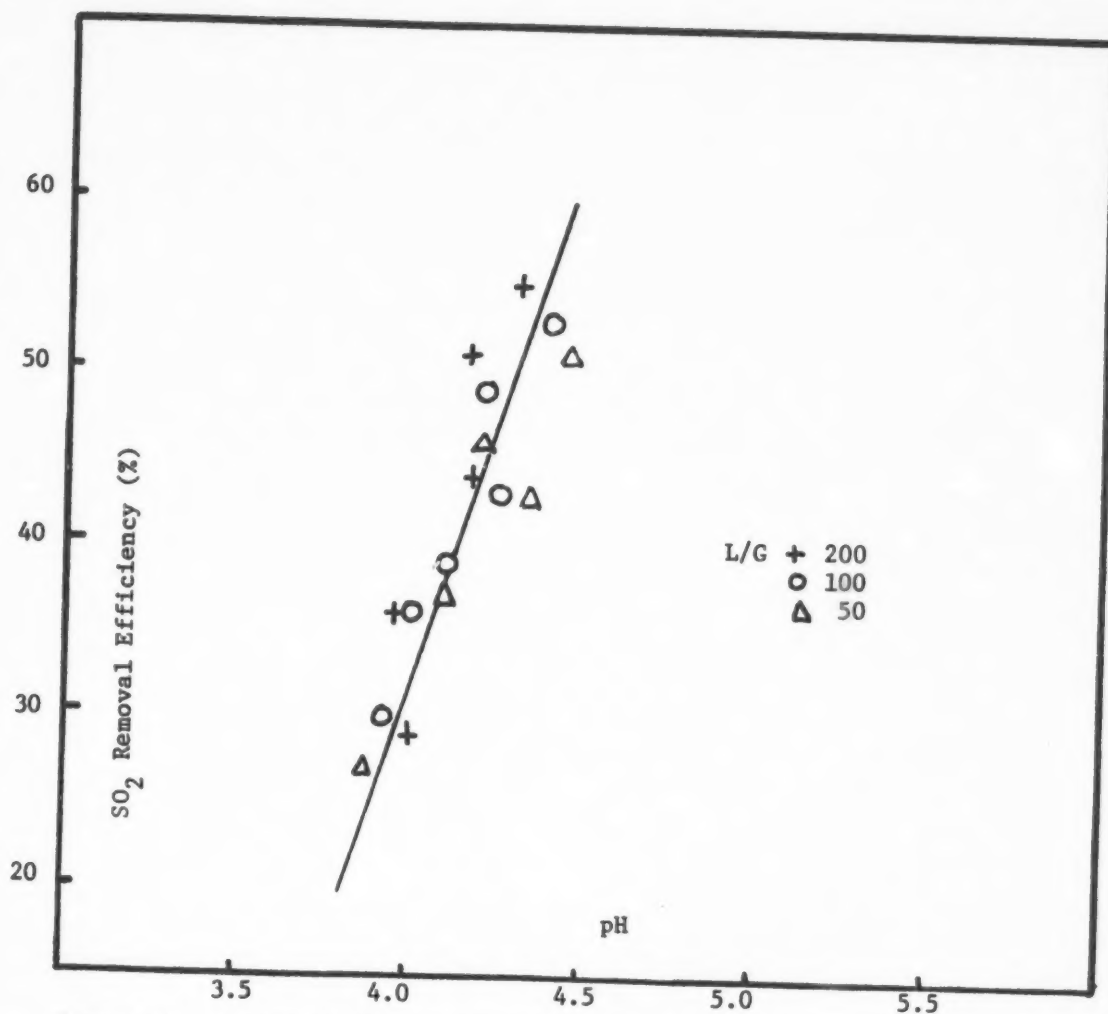


Figure 29. Sulfur Dioxide Removal Efficiency as a Function of pH-- 0.5% CaSO₃ (125°F, No Oxygen)

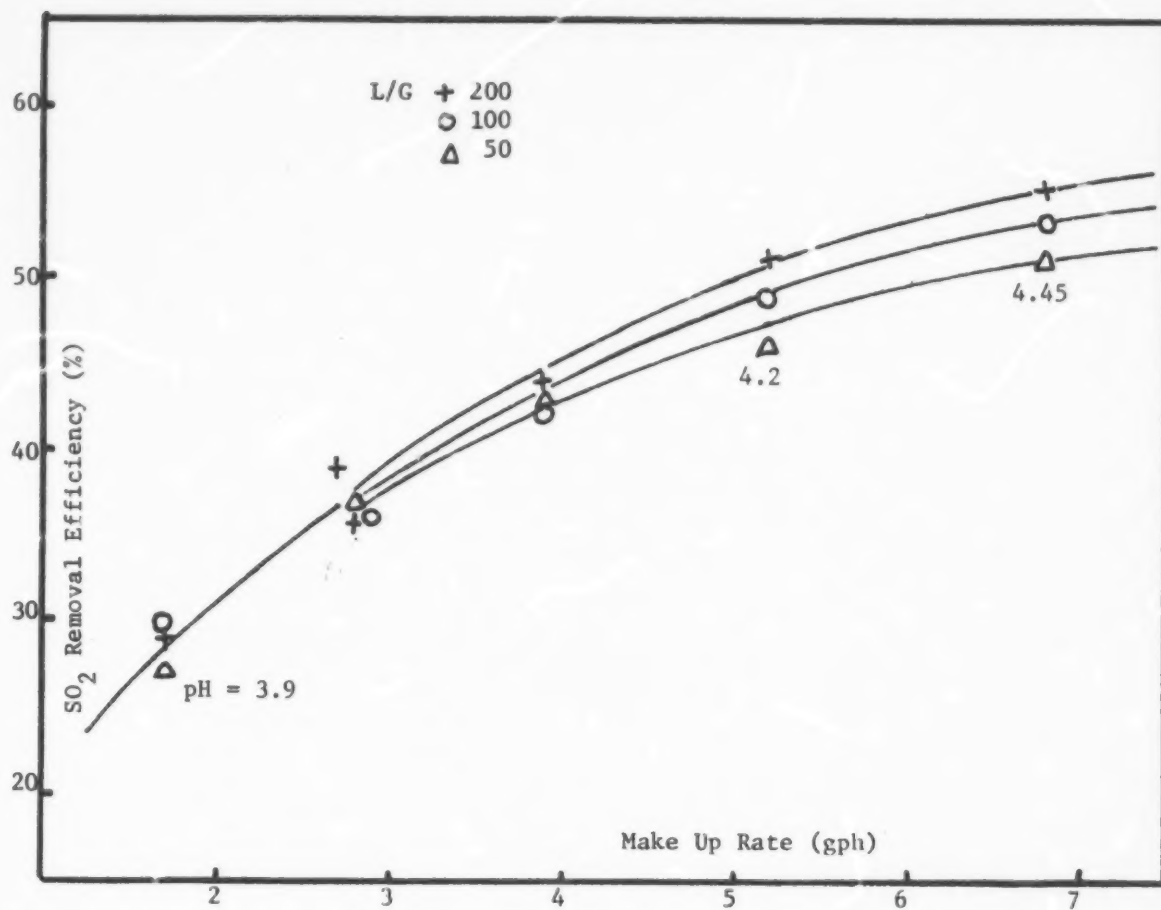


Figure 30. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate -- 0.5% CaSO₃ (125°F, No Oxygen)

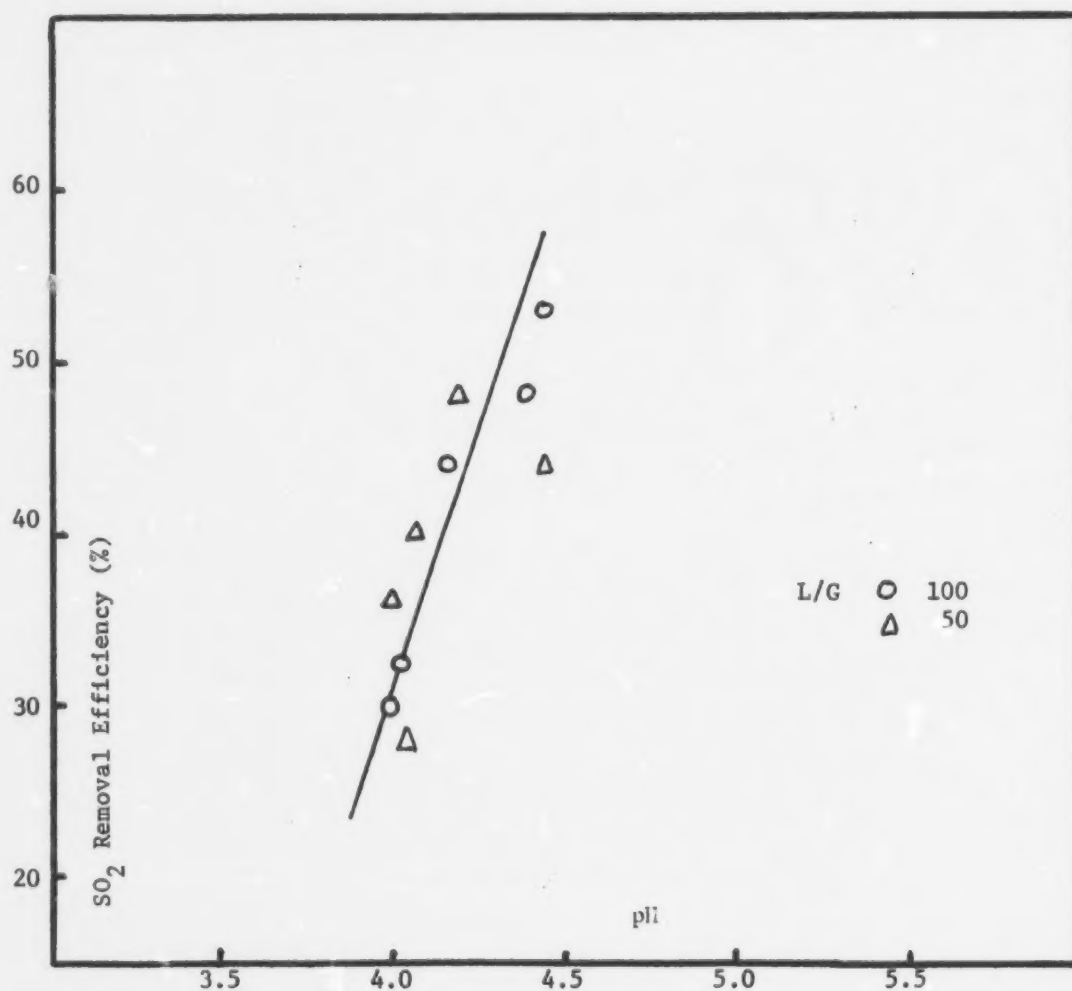


Figure 31. Sulfur Dioxide Removal Efficiency as a Function of pH-- 0.5% CaSO₃ (125°F, 4% Oxygen)

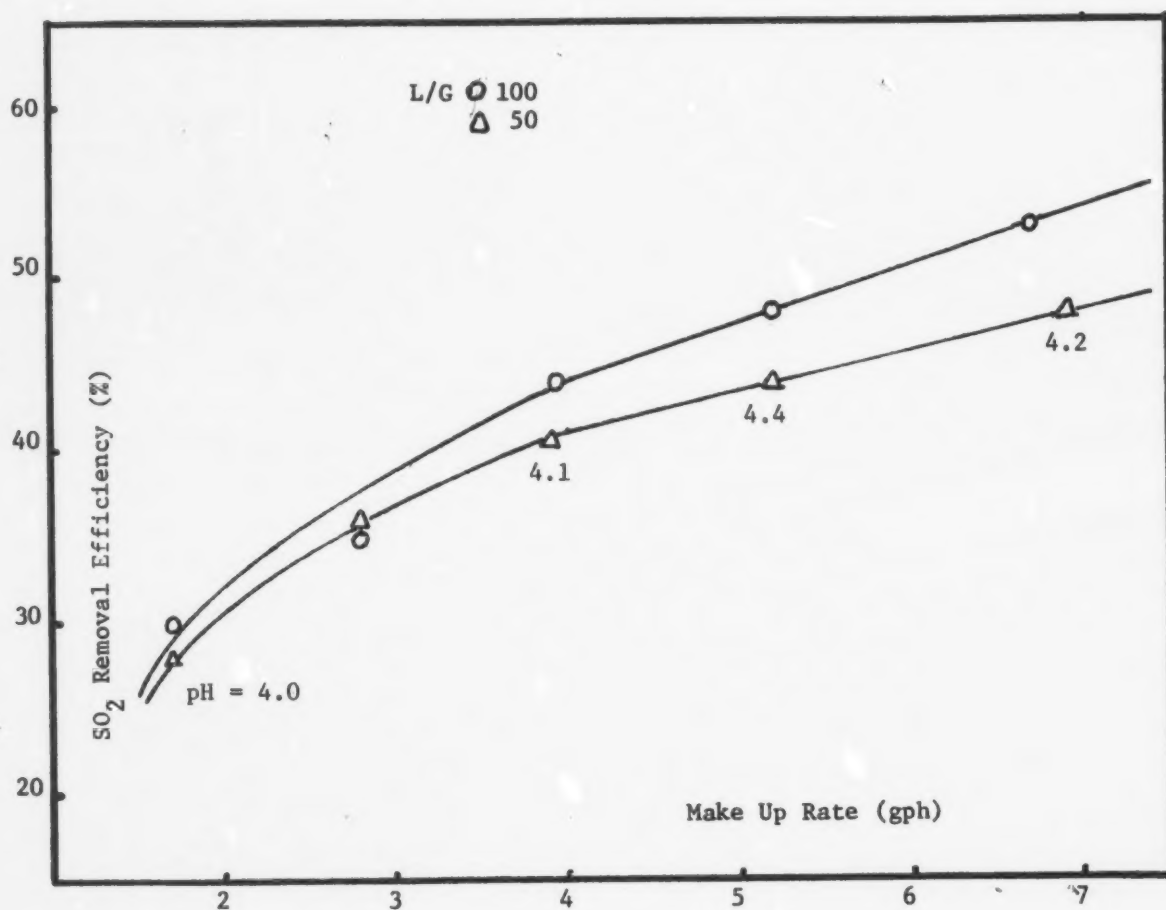


Figure 32. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate --
0.5% CaSO₃ (125°F, 4% Oxygen)

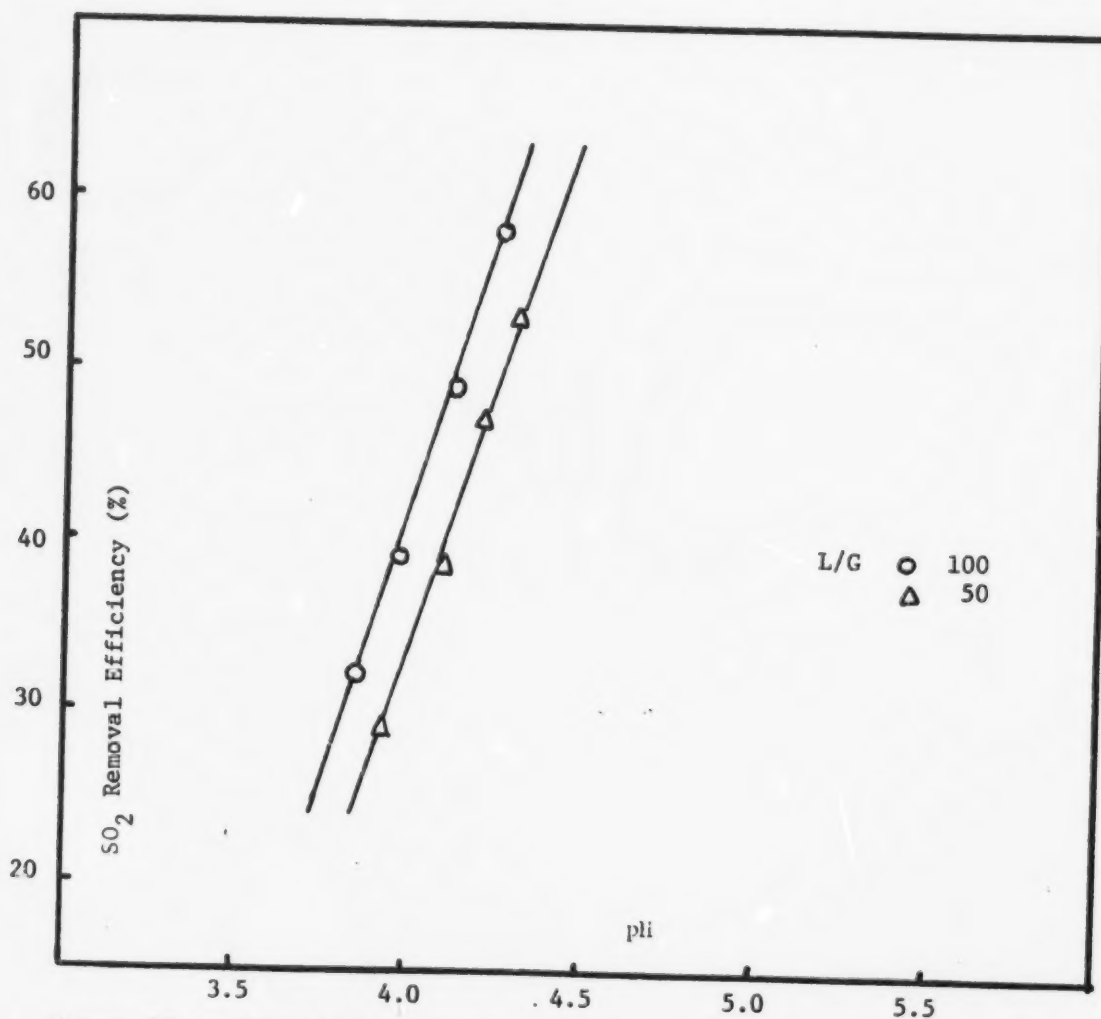


Figure 33. Sulfur Dioxide Removal Efficiency as a Function of pH-- 0.5% CaSO₃ (100°F, 4% Oxygen)

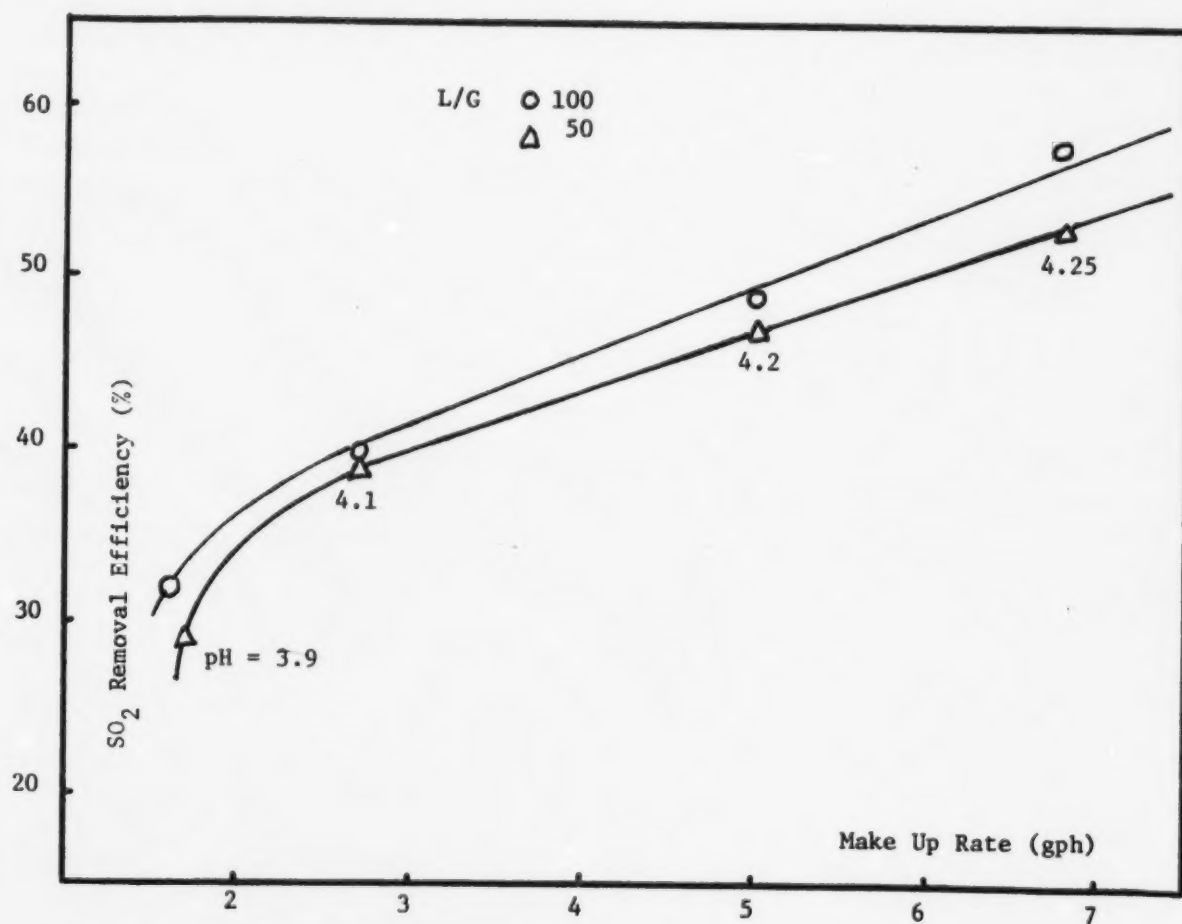


Figure 34. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate--
0.5% CaSO₃ (100°F, 4% Oxygen)

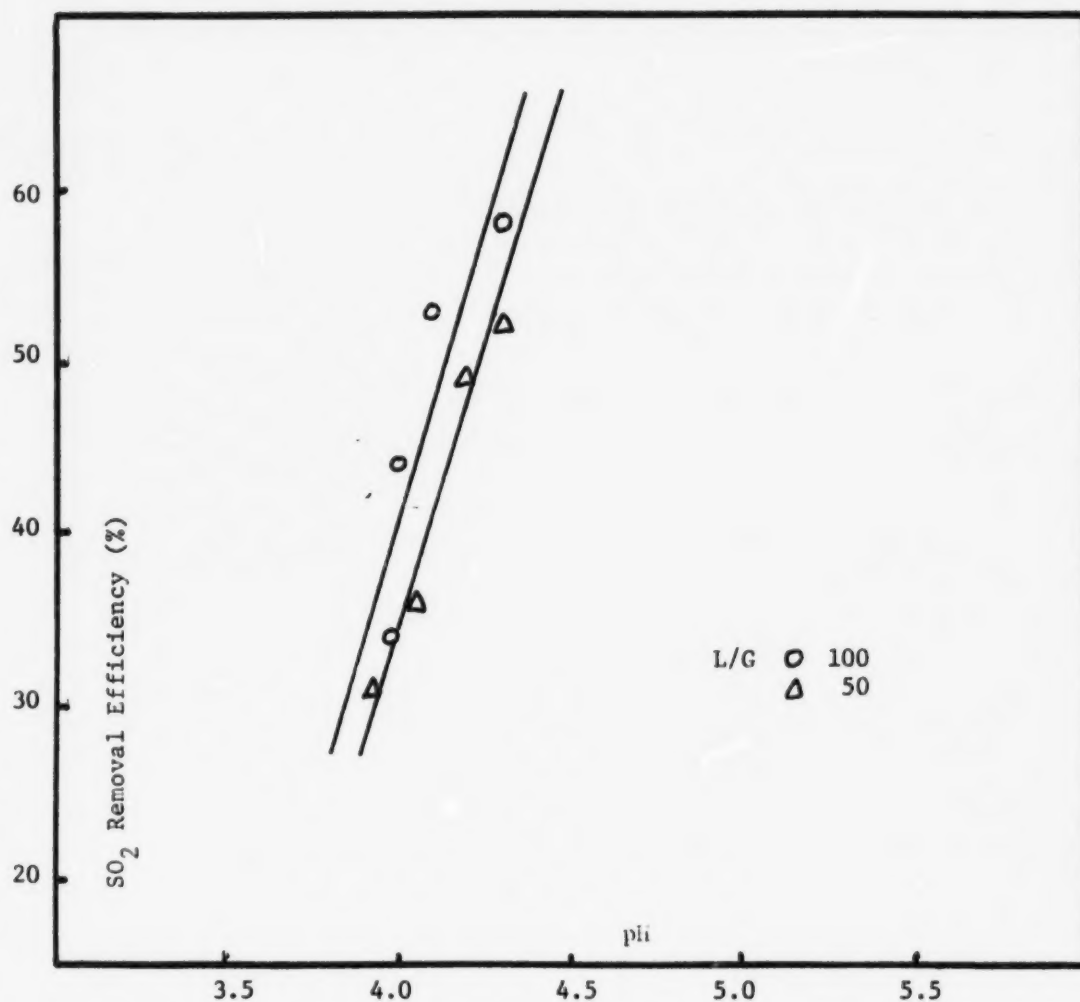


Figure 35. Sulfur Dioxide Removal Efficiency as a Function of pH--
0.5% CaSO₃ (100°F, 4% Oxygen, 13% Carbon Dioxide)

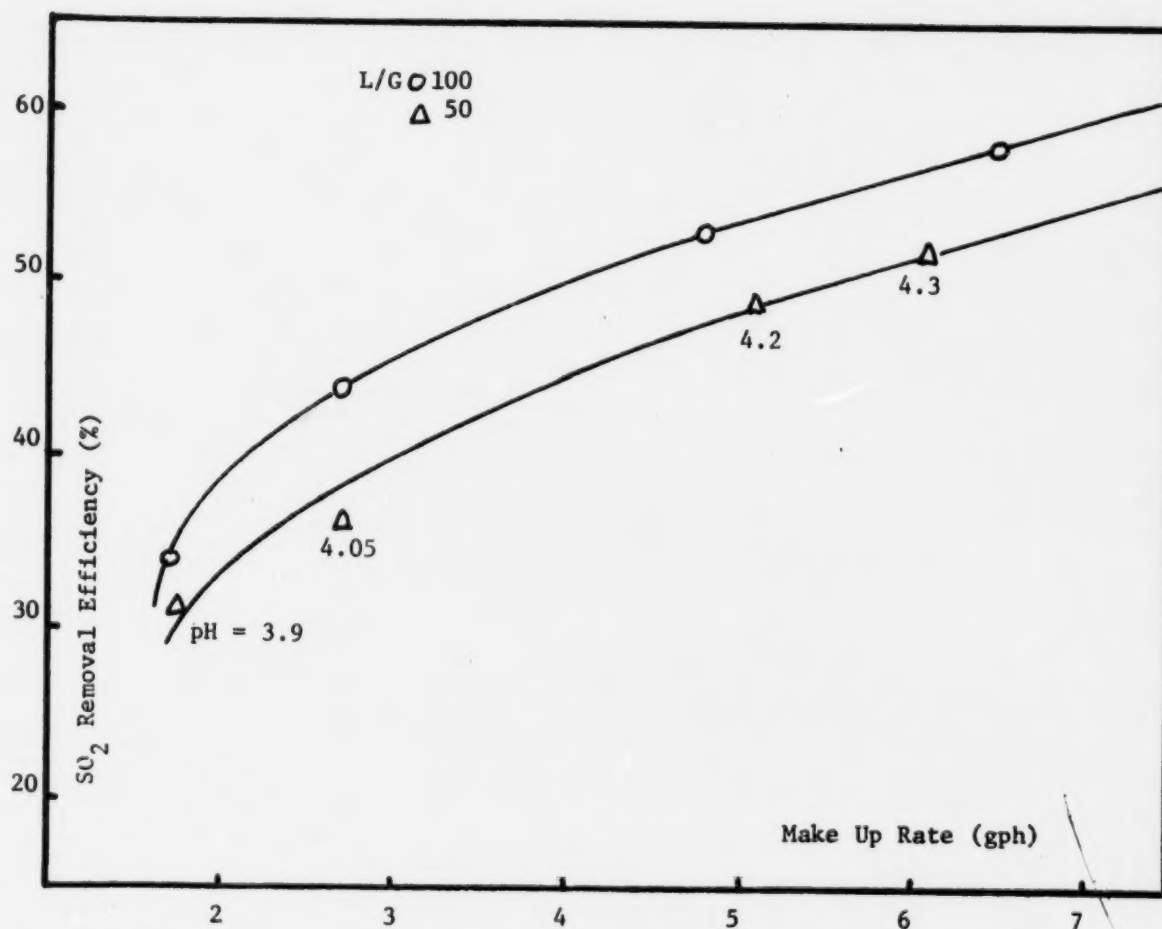


Figure 36. Sulfur Dioxide Removal Efficiency as a Function of Make Up Rate --
0.5% CaSO_3 (100°F, 4% Oxygen, 13 % Carbon Dioxide)

Scaling Experience

During a total time on-line of about 65 hours, there was no cumulative pressure drop increase (Figure 37). No precipitation or scale formation was expected during run XXVI at 125°F because of the absence of oxygen in the gas stream and carbonate species in the liquor. Runs XXVII-XXIX, on the other hand, were carried out in the presence of oxygen; and qualitative analysis showed the presence of sulfate. Nonetheless, after 65 hours operation no evidence of precipitation or scaling on the column packing or any other part of the apparatus was observed. This contrasts markedly with the introduction of oxygen into a carbonate slurry system where catastrophic scaling occurred after about 12 hours.

In general, the pH is much lower under a given set of process conditions with sulfite than with carbonate slurries and can be quite close to the equilibrium value for a sulfite slurry.

Slurry Analysis and Mass Balance

Analysis of the slurry for sulfite and for calcium at the inlet (make up) and exit (purge) has been made for each set of steady-state conditions. These results are presented in Tables XV-XXIX together with the sulfur dioxide removal data.

At steady state, the calcium and sulfite balances for runs made in the absence of oxygen should be zero. The deviations from zero are therefore indicative of a non-steady state in the solids being circulated in the scrubber due to solids hold-up and scale deposition. The sulfite and calcium balances tend to show smaller negative values at high liquid rates when solids deposition in the column is less pronounced.

Sulfite losses should be equal to calcium losses if the net reaction is formation and hold-up of calcium sulfite. Average values for runs made in the absence of oxygen give good agreement although individual samples show some scatter. For runs where oxygen was present, the oxidation of sulfite to sulfate must be taken into account in computing a sulfur balance.

For runs made with the 0.5% CaSO_3 slurry (Tables XXVI-XXIX), the average calcium balance is close to zero as expected because there is no net precipitation in the scrubber. (Absorption of SO_2 leads to $\text{Ca}(\text{HSO}_3)_2$ formation.) The variations recorded for individual analytical results can probably be ascribed to mechanical hold up in the apparatus (and experimental error). The calcium analysis shows that a very good mass balance can be obtained with the apparatus under conditions where no precipitation or scaling is occurring.

Results for the sulfite balance show a consistent negative error which cannot be due to precipitation in the scrubber as in runs with carbonate slurries. Some of the discrepancy could be due to sulfate

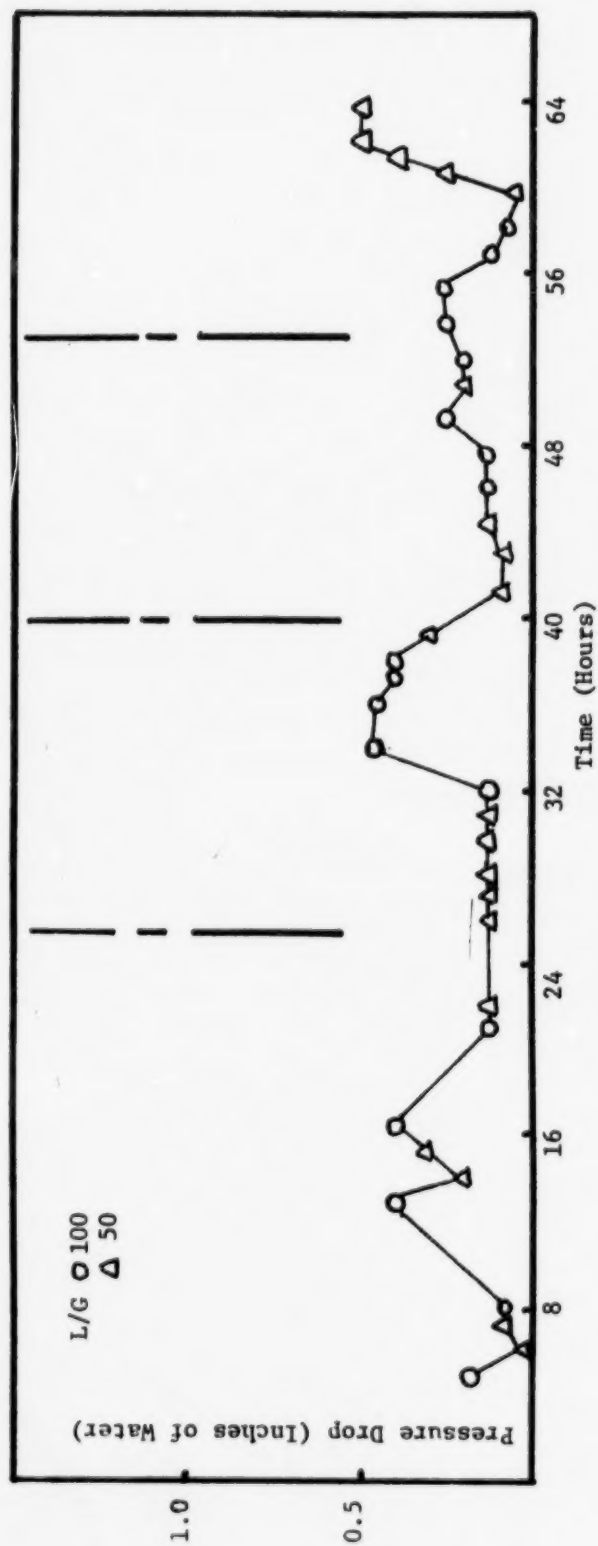


Figure 37. Pressure Drop as a Function of Operating Time -- 0.5% CaSO_3 .

formation in runs XXVII to XXIX. However, oxygen was not present in run XXVI and the sulfite balance shows a large negative value.

Examination of the data also shows that the values of calcium to sulfite in solution approach a 1:1 ratio rather than the 1:2 ratio expected for calcium bisulfite. The sulfite and calcium values are both in excess of the predicted equilibrium values which either indicate a supersaturated solution of calcium sulfite or incorrect assumptions in the thermodynamic calculation.

Various checks were carried out on the analytical method for sulfite and the sampling technique to discover the source of any errors contributing to the sulfur losses. Samples have been fixed with potassium hydroxide to prevent loss of SO_2 from the solutions while handling. Samples have also been analyzed immediately on removal from the apparatus. In each case the results were within experimental error (5%) of control samples. Tests for thiosulfate were also negative.

The negative sulfite balance also appears related to the experimental variables such as L/G ratio and SO_2 removal efficiency. One possible explanation of the loss of sulfite is evolution of SO_2 in the hold tank, where the residence time is 4-16 minutes, before the analytical sample is taken. This evolution of SO_2 may be quite significant at the low pH obtained in CaSO_3 slurries but would be much smaller in CaCO_3 slurries.

For the runs summarized in Tables XV-XXV, the average sulfite losses are about the same for all runs, ranging from 17.6 to 18.7 m.moles/l. There is also good agreement for the calcium balance, except for a somewhat lower value in run XVIII. Therefore the losses appear to be independent of temperature and calcium carbonate concentration. The sulfite loss is consistently greater than the calcium loss by a small amount and may be due to loss of SO_2 from the hold tank before sampling.

The equilibrium concentration of sulfite ion in solution varies with pH, falling rapidly above pH 6. Calcium in solution also falls with increasing pH and reaches the calculated thermodynamic equilibrium value at about pH 6. Below pH 5.5 the concentration of calcium is only slightly less than that of sulfite and the concentration of sulfite in solution seems consistently higher than indicated by the calculated thermodynamic curves.

In Tables XXVII and XXVIII, for runs with a calcium sulfite slurry in the presence of oxygen, there is essentially no calcium ion lost in either run. Therefore the negative sulfite balance should be largely accounted for by the conversion of sulfite to sulfate, in the scrubber. As the results show, the average total sulfate concentration exceeds the sulfite loss by a considerable amount. At present there is no satisfactory explanation of this anomaly but it may be due to difficulties with the gravimetric determination. Alternative analytical methods are being investigated for future work. The concentration of sulfate in solution

is indicative of a saturated solution. Since the samples had been allowed to equilibrate in the presence of CaSO_4 , supersaturated solutions would not be expected.

DISCUSSION

Effect of Operating Variables on SO_2 Removal Efficiency (No Oxygen)

Experiments have been carried out as described above to define the scrubbing efficiency and scaling potential of calcium carbonate, limestone, and calcium sulfite slurries as a function of various operating parameters such as liquid to gas ratio (L/G), stoichiometry of calcium carbonate or limestone addition, temperature and slurry concentration. Derivative parameters such as steady state pH in the effluent hold tank purge stream and SO_2 removal rates were recorded.

The extent of scaling was observed primarily by the increasing pressure drop across the packed bed scrubber, by visual observation of deposits in the rest of the scrubber loop, and from mass balance results. These observations are discussed later.

In Figure 38 we display the proportion of sulfur dioxide removed from the gas stream as a function of effluent hold tank pH. A feed of 0.5% calcium sulfite slurry gave pH values below 4.3; an 0.5% calcium carbonate slurry gave pH values between 4.3 and 6.4 and a 1% calcium carbonate slurry gave operating pHs in excess of 6.4. Equipment limitations in the bench scale scrubber prevent us from operating in the same regions of pH with these different slurry feeds. However, we believe that the results represent a continuous series of scrubber loop conditions across the pH range 3.7 to 6.6.

Superficial inspection of Figure 38 makes it clear that the kinetic and equilibrium conditions in the scrubber are a complex function of pH (and stoichiometry), temperature, and L/G. At different ranges of pH, different mechanism are in operation. Insights into the scrubber mechanisms may be obtained by considering the effect of three variables on scrubber performance.

pH

The rate of sulfur dioxide removal is clearly a strong function of pH and in all regions increases linearly with increasing pH. However, in the pH region below 4.3 and above 6.6, the SO_2 removal rate is a stronger function of pH than it is in the region between 4.3 and 6.4.

In our experiments, the effects of stoichiometry cannot be distinguished from the effects of pH, since changing stoichiometry also changes pH. pH is recognized to be an important variable in equilibria and kinetic

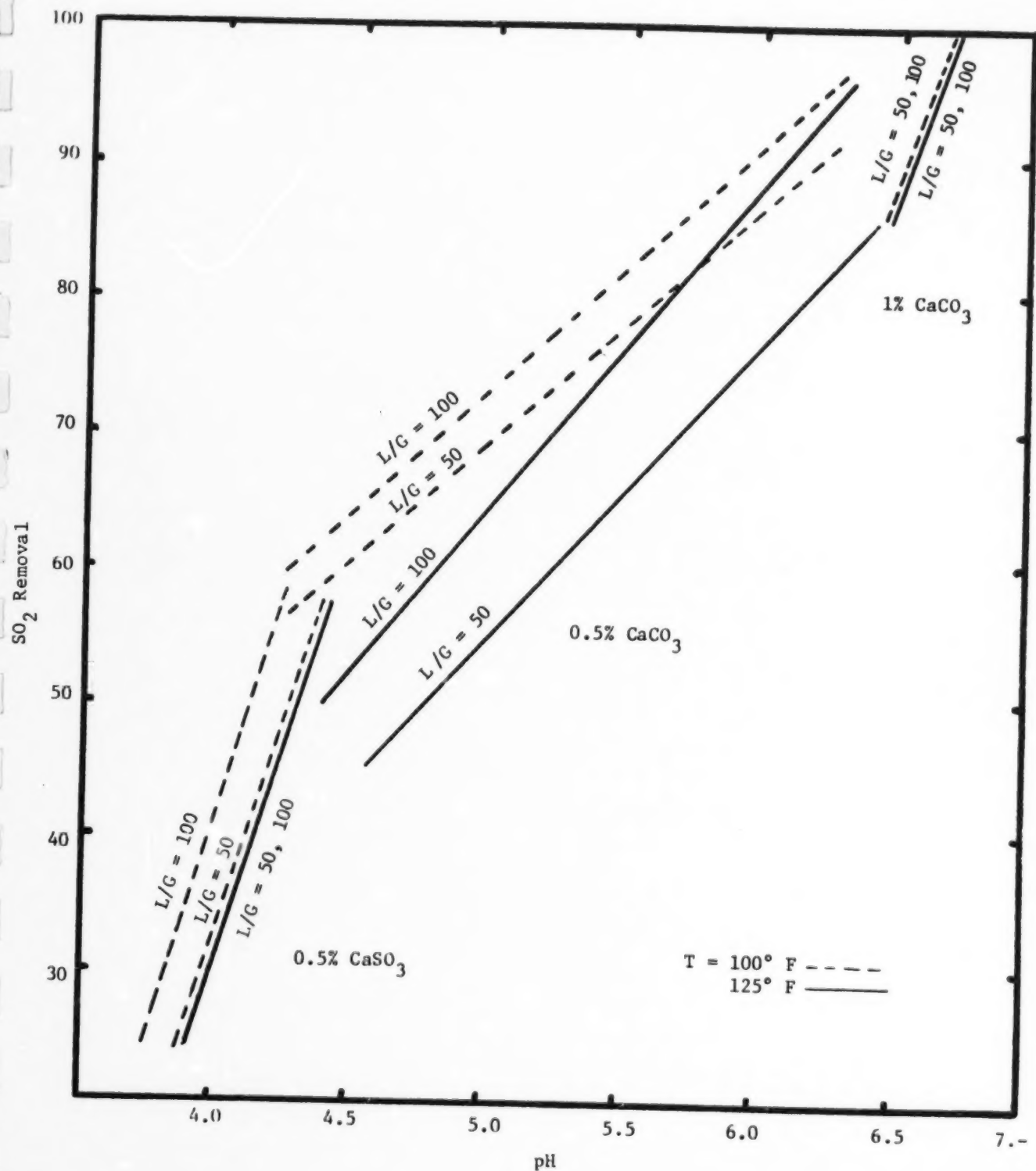


FIGURE 38
EFFECT OF pH ON SO₂ REMOVAL FOR DIFFERENT SLURRIES
 (No Oxygen)

factors. The SO_2 removal rate is high at a stoichiometry down to about 0.8 which corresponds to almost complete carbonate utilization. The removal rate drops off rapidly at lower stoichiometries and the pH also falls rapidly. Stoichiometries greater than 1 increase the SO_2 removal rate to a small extent.

L/G

In general, if absorption efficiency of a gas liquid contactor increases with L/G it can be deduced that the reaction is kinetically limited by a liquid phase reaction: the more liquid which is supplied to the scrubber in comparison to the gas flow the less is this factor limiting on the total rate of reaction. Referring again to Figure 38 it is clear that L/G has a strong effect in some regions of pH and at some temperatures but not at others. Thus, under some conditions, scrubber kinetics are limited by liquid phase reactions; under other conditions other rate limiting steps become important.

Temperature

In most instances the rate of chemical and diffusion reactions is expected to increase with temperature. Referring to Figure 38, we see that in some regions of pH and at some values of L/G lowering the temperature of the scrubber liquor from 125°F increases the SO_2 removal rate. The factor which may be responsible for this negative temperature effect is the equilibrium partial pressure of sulfur dioxide above the scrubber liquor which would be expected to decrease as the temperature falls. Thus in those regions where a negative temperature effect is observed, we suppose that the partial pressure of SO_2 above the liquor is in some way rate limiting in the absorption of SO_2 from the gas stream.

Kinetic Observations

The observed effects cannot yet be fully rationalized to yield a mechanistic understanding of the kinetics of the scrubber process. However, it is possible to make some general observations on the mechanisms which may be rate controlling in the various pH ranges.

pH Less than 4.3 (0.5% Calcium Sulfite Slurry)

In this pH range the overall mechanism of SO_2 removal from the gas stream involves reaction with solid calcium sulfite to produce a calcium bisulfite solution. This reaction results in a low steady state pH.

At an L/G of 100, a decrease in temperature from 125°F to 100°F increases the rate of SO_2 removal. This inverse temperature coefficient is attributed to a lower partial pressure of sulfur dioxide above the liquid phase at the lower temperature. At 125°F, there is no L/G effect on the total reaction rate indicating the absence of diffusional limitations in the liquid phase over the pH range. However at 100°F, the higher SO_2 interfacial reaction rate (due to the more favorable equilibrium) makes the liquid phase resistance important and there is an increase in total reaction rate by increasing the L/G from 50 to 100.

pH 4.3 to 6.4 (0.5% Calcium Carbonate Slurry)

In this region we observe both an effect of L/G at 100°F and 125°F and a negative temperature effect upon the reaction rate. The steady state kinetically limiting reaction mechanism must therefore involve a change in sulfur dioxide partial pressure above the liquor and a subsequent diffusion (or reaction, but this is unlikely) in the liquid phase.

Note that as the pH increases at an L/G of 100 and 50 the negative temperature effect becomes less marked as the SO₂ partial pressure above the liquor falls because of the rising pH. Also, in this pH range the bicarbonate concentration increases in the scrubber liquor as the pH rises. Thus bicarbonate ion concentration may be contributing to the rise in SO₂ removal as a function of pH. In this pH region (at least up to pH 6), ² equilibrium calculations show that calcium carbonate is not stable as a solid phase if CO₂ is less than one atmosphere and all carbonate species should be in solution.

pH Greater than 6.4 (1% Calcium Carbonate Slurry)

In this region we see no L/G effect and no temperature effect on the reaction rate. However, the reaction rate is as strongly dependent on the pH as it was below pH 4.3. In this region we again have a reaction which is dependent on the dissolution of a solid phase (calcium carbonate) as absorption of SO₂ occurs. Clearly the equilibrium SO₂ partial pressure above the liquid is no longer rate controlling (the equilibrium pressures are exceedingly low) and apparently liquid phase resistances, despite the high rate of reaction, are absent. Therefore, the reaction rate must be close to the gas phase limitation (as is observed with highly alkaline scrubbing media - see preliminary shakedown experiments), and controlled by the reaction or production of a chemical species whose concentration is solely and strongly dependent on pH (for example, carbonate or bicarbonate).

If the rate of dissolution of the carbonate is an important kinetic factor in determining the rate of reaction in this pH region, one might expect the removal rate vs pH line to be shifted to lower pH levels with more difficulty dissolving limestones.

Of particular importance to practical scrubber operation is the fact that the results shown in Figure 38 indicate, just as the equilibrium calculations of Chapter II also do, that the pH range of normal scrubber operation lies in a complex region of equilibrium and kinetic effects. In the range of pH from 5.7 to 6.5, radical changes in the effect of all the operating variables - L/G, temperature, and pH - are observed. Slight changes in operating conditions can give very different results in regard to SO₂ removal efficiency and, by implication, to scaling reactions. Also, pH is a strong indication of overall scrubber operating conditions.

Scaling Phenomena

Types of Scale

Several different types of scale were observed during the course of operation of the bench-scale scrubber, corresponding to scale observed in the field. Very early in the program, a thin hard sulfite scale with a yellow surface coloration was observed to form on some of the glass surfaces of the apparatus. This type of scale was formed when scrubbing with either calcium carbonate or limestone, although the color was slightly different in the two cases.

Gas inlet deposits, consisting of a mixture of calcium sulfite, calcium sulfate, and calcium carbonate, were formed, but in contrast to larger units the deposits never built up to a troublesome level under the relatively low flow rate conditions used.

Sulfite scale built up gradually during runs made in the absence of oxygen, as evidenced by a slow increase in pressure drop across the packed bed, as well as negative calcium and sulfite mass balance results. The sulfite scale build-up is more rapid at 125°F than at 100°F. At the higher temperature, the pressure drop increase forced a shut-down of the apparatus in 20 hours, while at 100°F, it was possible to run for 30 hours. The sulfite scale collected primarily on the packed bed and on the walls below, but some scale also precipitated in the hold tank and in the scrubber recycle loop. Scale deposition on the packed bed, because of increased liquid hold up (as shown by pressure drop increase) tends to improve removal efficiency.

The presence of 4% oxygen, and hence the conversion of some sulfite to sulfate, led to catastrophic scaling when scrubbing with limestone. At 125°F, the scrubber plugged up rapidly and without warning after 12 hours of operating time. During that time, removal efficiency was unaffected and the change in pressure drop across the column was minimal. In fact, the severe scale deposition occurred mainly in the recycle lines, with very little deposition on the packed bed itself. The material responsible for the catastrophic plugging proved to be a mixture of calcium sulfate, sulfite, and carbonate. Since oxygen was clearly implicated in the scaling reaction, it is possible that sulfate deposition is responsible for initiating a cementing action.

Effect of Materials of Construction

In order to qualitatively evaluate the scaling potential for various operating parameters, coupons of various materials were immersed in the scrubber at six separate locations for a total of 37 1/4 hours of run time. Major experimental parameters included 1/2% CaCO₃, 4% O₂, 2300 ppm SO₂ and liquid temperatures of 125°F and 100°F.

Half-inch square by 1/16 inch thick samples were employed of Monel 400, Teflon, Copper (OFHC), 316 Stainless, low carbon steel (1008) and borosilicate glass. One surface of the sample was polished and the other was abraded on 240 grit SiC paper. Samples were linked together in a chain with nylon thread. The individual coupons and the composite chain were tared to the nearest tenth milligram.

Specimen chains were placed at six positions as follows:

- T₁ - In line from holding tank to makeup tank
- T₂ - In makeup tank
- T₃ - In line from makeup tank to scrubber
- T₄ - Top of scrubber
- T₅ - Just below bed (at gas inlet)
- T₆ - In holding tank

Examination of the sample chains after exposure showed no evidence of any scaling, corrosion or staining of the teflon, glass or stainless steel coupons. The monel coupons were tarnished in all cases, but showed a weight change of no more than a few mg; there was no evidence of scale formation. The copper coupons were all tarnished, some quite heavily. Samples from positions 3 and 5 contained very small amounts of white-colored scale.

Finally, the low carbon steel samples were all heavily corroded (oxidized). A white-to-dark gray scale was observed on samples at positions 1, 2, and 6. The other samples were very heavily corroded which may have precluded the formation of a scale. Weight changes for the low carbon steel and copper samples are as follows:

<u>Sample Position</u>	<u>Weight Loss - mg</u>	
	<u>Low Carbon Steel</u>	<u>Copper</u>
1	7	3
2	7	21
3	24*	11
4	15*	23
5	372	10
6	18	4

*Weight gain - mg

X-ray diffraction patterns were obtained from the copper and low carbon steel samples that appeared to have scaled; these samples included low carbon steel, positions 1, 2 and 6, and copper, positions 3 and 6. In all cases, the scale was found to be $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$. There was not evidence for any transformation to sulfate.

It is difficult to account for the loss in weight of the copper coupons. Presumably, the relatively low pH of the solution resulted in some dissolution of copper. The final weight of the low carbon steel samples, of course, is a compromise between the weight loss due to formation of a (mostly) non-adherent oxide versus the weight gain due to scale formation.

In all cases the observed scale was very loosely adherent, being easily removed with a scraper.

CHAPTER IV

POTENTIAL SCALE CONTROL METHODS

On the combined bases of the literature review, thermodynamic analyses, and supplemental experimental work carried out over the past year, we have assessed the potential effectiveness of scale control methods that have been applied to wet scrubbers; we have identified some of the critical factors which seem to influence scale formation; and we have identified a number of approaches to scale control which merit further exploration.

SUMMARY

Many of the basic principles involved in designing and operating limestone wet scrubbers to minimize scaling problems are well recognized and may be summarized as follows.

1. Good Engineering Design

In scrubber towers wherein a gas is to be in intimate contact with a liquid flowing countercurrently, it is imperative to design and operate the unit in such a manner so as to preclude any appreciable by-passing of the two streams. Ordinarily this is accomplished by feeding both the liquid and gas evenly over the tower cross section, and in some cases, by collecting and redistributing the streams at one or more heights within the column.

In the limestone tail-end addition systems of interest here, the appreciable solids content in the liquid stream presents an additional complication. With solids flow, a good distribution of the gas, liquid, and solid portions is even more important since solids may become so concentrated in certain zones as to form deposits that can grow and disturb the efficient operation of the column, even to the extent of complete blockage.

While the critical velocities needed to keep particles in suspension are lower than those normally encountered in scrubbers, especially in the case of vertical flow, areas of deceleration and possibly stagnation may form behind sections of packing, at bends in the piping, and at any areas of roughness in the pipe. It is in these areas that scaling could well begin by growth of crystallites onto the surfaces of mechanically deposited silt. Thus, any bends in the piping should be made with large radii of curvature; valves other than gate valves should be avoided; smooth piping should be used; obstacles in the flow path (uneven pipe joints, unnecessary valves, probes) must be eliminated; and abrupt changes in pipe diameter in the piping system should be avoided.

2. Avoidance of Intermittently Wet and Dried Areas

Experience has amply demonstrated that all surfaces exposed to the scrubber slurry should be well irrigated.

Gas inlet deposits, which have plagued most scrubber units, at least in the initial phases of operation, can generally be controlled by a combination of mechanical removal methods and inlet design modification.

Demister and reheater deposits have proved to be a more difficult problem. Effective demister wash systems are not always practicable, and periodic mechanical cleaning seems at present to be unavoidable.

3. pH Control

The solubility of calcium sulfite increases sharply above pH 6. When $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ is formed by the absorption reaction ($\text{CaCO}_3 + \text{SO}_2 + 1/2\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$) above pH 6, the potential for sulfite scaling is very great. At pH levels below 6, a considerable amount of the sulfite formed can remain in solution as bisulfite. The experiments discussed in Chapter III suggest that SO_2 removal efficiencies of 80 - 90% can be achieved down to pH 5.7 or 5.8 at the bottom of the scrubber. Efficiency falls off rapidly at lower pH levels. If for any reason, there are local increases in pH above 6 in the scrubber proper, precipitation of calcium sulfite, and eventual scaling may be anticipated.

4. High L/G

It has been found empirically that increases in L/G have a beneficial effect on reducing the rate of scale deposition. At least two mechanisms may be operative. High liquid flow rates might simply provide a mechanical flushing of surfaces where deposits might otherwise form. In addition, the make per pass is inversely proportional to L/G. The lower the make per pass, the lower the potential degree of supersaturation, and hence, the less likelihood there is for chemical scaling. In the work carried out at ICI in the 1930's, the safe make per pass was found empirically to be in the neighborhood of 4-5 millieq/l of total sulfur. In order to maintain such a low make per pass in modern scrubbing units, L/G would have to be well over 100, an intolerably high slurry circulation rate from the point of view of pumping load.

5. Seeding

The use of seed crystals to dissipate supersaturation is a venerable scale control technique. The levels found by ICI to be effective in wet scrubbing, 3-5% each of calcium sulfite and calcium sulfate in the slurry, are far higher than the concentrations normally required. Since a high solids content in the slurry does tax the pumps, we would recommend that optimum seed concentrations be established empirically for typical

modern scrubber operating conditions. While the effectiveness of gypsum seed crystals for dissipation of calcium sulfate supersaturation has been demonstrated in the laboratory, the usefulness of calcium sulfite seed crystals has never been definitively established. In the review of scale control techniques used in industrial processes, which concludes this chapter, we discuss some of the fundamental factors related to optimum choice of seed concentration and structure.

6. High Residence Time in Hold Tank

A delay tank or hold tank is normally introduced into the scrubber loop to allow sufficient time to desupersaturate scrubber liquors before they are returned to the scrubbing tower. Addition of fresh calcium carbonate to the scrubber effluent liquor just before it enters the hold tank further aids in dissipating any sulfite supersaturation, since an increase in pH promotes precipitation of calcium sulfite. The required delay times to assure desupersaturation under given scrubber operating conditions have not been well-established. ICI provided for a three to four minute delay time, but limited the sulfite-sulfate make per pass to 3-4 millieq/l. Delay times of 10-20 minutes are more common in modern practice, but the make per pass is typically much higher.

7. Temperature Control

Although the options for controlling scrubber liquor temperature are limited in practice, our work suggests that scaling problems are considerably less acute at 100°F than at 125°F. The rate of deposition of calcium sulfite appears to be more rapid at the higher temperature. In addition, the equilibrium transition point between gypsum and anhydrite lies at 100°F. At higher temperatures, a deposit of the stable anhydrite or the metastable hemihydrate (plaster of paris) on process equipment surfaces, might initiate a cement forming or "setting" reaction that could lead to catastrophic scaling. It thus may be advantageous to operate wet scrubbers at temperatures below 100°F if at all practicable.

8. Control of Oxidation

While oxidation clearly plays a role in calcium sulfate scaling, the optimum degree of oxidation for minimum scaling is unknown. On the one hand, a high degree of oxidation might assure a steady supply of seed crystals for dissipation of supersaturation. On the other hand, sulfate scale is much more difficult to remove than sulfite scale, and it therefore might be desirable to inhibit oxidation. The extent to which oxidation can be catalyzed or inhibited, so that potential benefits might be determined, merits further investigation.

9. Use of Additives

Threshold additives of polyphosphates and polyacrylates have been used to control scaling in many industrial processes, but have not been explored for wet scrubbers. In the literature review which follows, the available data on the use of additives for scale control are discussed. Although none of the data were obtained under the precise conditions characteristic of wet scrubbers, threshold additives do appear to hold sufficient promise for reducing scale deposition rates in this application to warrant some investigation.

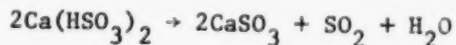
SCALE CONTROL TECHNIQUES USED IN INDUSTRIAL PROCESSES

Many industrial processes have been afflicted by deposition of calcium and magnesium scales from aqueous process streams. Research has been conducted by a variety of groups to devise operating procedures which minimize this problem. Advances have been made in many fields in the understanding of scale deposition processes and hence in the development of largely successful scale prevention techniques. While in many cases the methods used are unique to the industrial process under consideration, the general technology provides an essential background of information for a rational approach to the solution of scaling problems in wet scrubbers. Moreover, it appears that in some cases the methods which have been found to be effective might be directly applied or adapted to wet scrubber operation. We should note however, that in many cases conditions of temperature and chemistry are not the same, and experimentation will be essential to evaluate approaches.

Scaling problems arise in almost any process where heat is being applied to solutions of calcium or magnesium salts. Such solutions may be process liquors, or natural fresh, brackish or salt water often used for cooling purposes. In cases where evaporative loss of water occurs, deposition of dissolved salts is expected as their solubility products are exceeded. However, this is by no means the only cause of salt precipitation which under appropriate conditions may lead to scaling on the walls of containing vessels. For example, natural waters usually contain quantities of dissolved calcium bicarbonate which, when heated decomposes to calcium carbonate which is sparingly soluble and precipitates:



In wet scrubber operation, this is also a possible scaling reaction. In addition the analogous sulfite reaction may occur:



particularly where calcium bisulfite solutions meet hot incoming gases. Furthermore, some salts have inverse solubility curves; that is, their solubility decreases with temperature. If such a salt is nearly saturated and the solution meets a hotter surface such as a heat exchanger tube in a boiler, the solubility of the salt at the surface may be exceeded at the surface and scale be deposited. Such a salt is calcium sulfate dihydrate above about 55°C., and also anhydrous sodium sulfate and sodium carbonate monohydrate. It seems unlikely in wet scrubber operation, however, that the region of temperature of inverse solubility for calcium sulfate is reached, unless perhaps in the region of the incoming hot flue gases.

The industrial processes in which scaling has been a problem are mainly those where evaporation of calcium solutions takes place. These include the following:

<u>Industry</u>	<u>Process with scaling problems</u>
Sulfur dioxide scrubbing from flue gas.	Gas liquid contactors and subsequent handling of liquors.
Distillation of brackish and sea water.	Brine evaporation. Cooling waters for the steam.
Sugar manufacture.	Evaporation of sugar solutions.
Salt manufacture.	Evaporation of concentrated brines containing calcium sulfate.
Calcium sulfate manufacture.	Evaporation of concentrated calcium sulfate solutions.
Sulfur processing.	
Paper manufacture.	Evaporation of "black liquors" containing calcium sulfite and sulfate.
Phosphate processing.	
Sodium sulfate manufacture.	Evaporation of saturated solutions for recrystallization.

Some of the methods which have been developed for scale prevention in these industries are either too specialized or otherwise inappropriate for application to the wet scrubbing problem. These include pretreatment of cooling water by softening or by acidification and probably the addition of physical scouring agents (such as Taprugge balls) to recirculating liquors. We will not discuss these further. Two methods for scale control of potential utility in wet scrubbing, however, are those of seeding and threshold treatment.

Scale Control by Seeding

Scale deposition is often a slow process usually taking place from supersaturated solutions. If supersaturation is minimized by the acceleration of the precipitation process away from the walls of the containing vessel, scaling can be avoided. It has been found that in some systems, this can be achieved by seeding the solution with particles of a particular type, preferably of the same polymorph as the precipitating species. Nucleation of crystallites is thereby enhanced, and precipitation is largely confined to the bulk of the solution. Even where crystallization still occurs on the walls of the vessel, it is often found that the deposits are softer and easier to remove.

Sodium Sulfate Manufacture - An early description of the evaluation of seeding to control scale occurs in a review of evaporator design for sodium sulfate manufacture⁽¹⁸⁾. Without seeding, scale of 3/8 inch thick

accumulated in less than an hour and the evaporator ceased to function; with recirculation of seed crystals, evaporator operation was unaltered even after 5 1/2 days. However, special pumps had to be designed to withstand the abrasive action of the seed crystals. Features included an extra large impellor and shaft, very large oil ring bearings, a long running fit casing between impellor housing and stuffing box, circulating fresh water around the shaft in front of the packing and a special grade of packing.

Early Sulfur Dioxide Wet Scrubbing - This work inspired the use of seeding to control scaling in one of the first sulfur dioxide wet scrubbing plants to be installed at Fulham Power Station, England by Howden-ICI 19-21. In an earlier installation at Battersea, Thames River water was used to absorb the sulfur dioxide as sulfurous acid. This became oxidized to sulfuric acid by the air and was returned to the river to be neutralized by the "natural alkalinity" of the river water. At Fulham*, such a simple process could not be used because the additional acid would have exceeded the river's assimilative capacity. A lime slurry was therefore used to scrub the gas. Lime improved the absorption efficiency from 45% to 75% and eventually to over 98% compared to water alone.

However, in preliminary experiments, "a serious difficulty" arose in the form of deposits of calcium sulfate scales containing traces of fly ash, calcium sulfite and calcium carbonate which completely blocked the pilot washing plant after 72 hours. Studies were made thereafter of the rate of desupersaturation of calcium sulfate solutions when seeded with different amounts of calcium sulfate dihydrate crystals.

This work showed that if supersaturation of calcium sulfate were to be limited in the scrubber and the total liquor capacity of the system were to be of reasonable size, a high proportion of solids in the recirculating liquors was necessary to seed the crystallization adequately (5% by weight of slurry or more). Actual times for the desupersaturation of solutions which had the necessary slight degree of supersaturation required to prevent scaling were longer than those shown in Figure 38, but similar seed concentrations were found effective. Stagnation at surfaces was found to encourage crystal attachment and was minimized, and the crystalline shape of the calcium sulfate was found to seriously limit the effectiveness of calcium sulfate seeding. Therefore, oxidation of sulfite to sulfate was encouraged by maintaining the pH below 6.4 so as to keep the sulfite in solution, while still maintaining high SO₂ scrubbing efficiency. The pH electrode had just been developed around the time that ICI was initiated. Therefore the numerical values of pH should probably not be taken too literally.

*Fulham Power Station was designed to liberate 1,000 million cu. ft. of flue gas per day containing 0.9 grain of SO₂ per cu. ft. In 1937, this was reduced by lime slurry scrubbing to only 0.0046 grains per cu. ft.

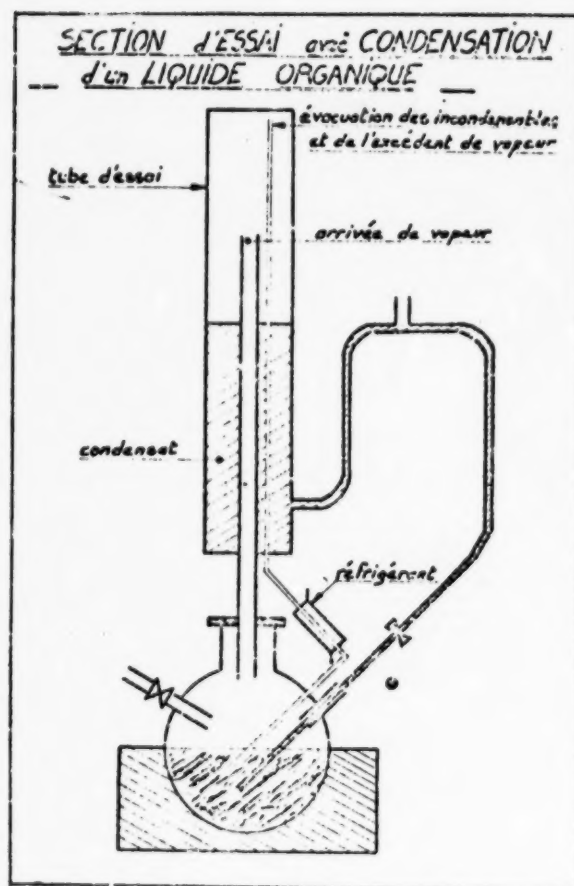
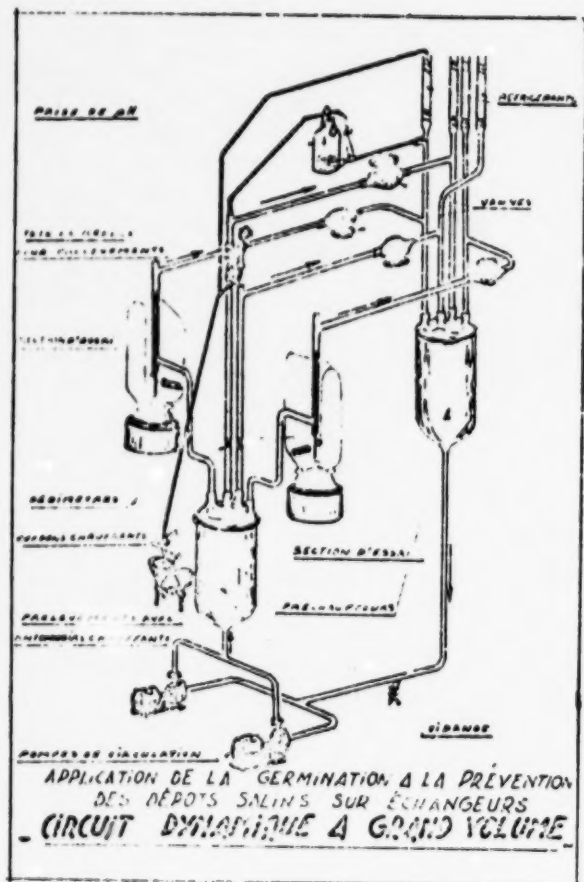
ICI found that calcium sulfite supersaturation was not a problem because of solubilization by the dropping pH in the scrubber, the oxidation of sulfite to sulfate and the proportion of make up liquor to liquor rate. With wood grid packing it was found that a delay time to allow precipitation external to the scrubber of 14 minutes per grain equivalent of sulfur per gallon absorbed and oxidized within the scrubber to calcium sulfate in one liquor cycle was adequate, when the suspended calcium sulfate was over 2.5% by weight (the scrubber operated at pH 6.8 - 6.3). A plant operated at Billingham under these conditions was found to be scale-free (despite bird's nests in the scrubber!) over a period of 3,500 hours.

The optimum procedure was therefore to use a slurry of lime or calcium carbonate containing 5% of calcium sulfate dihydrate, intermittent flushing (to prevent deposition in stagnant regions), pH control, a chamber for oxidation of sulfite to sulfate, and settling chamber. This process was patented in 1937.²²

Paper Industry

Several other successful uses of seeding to control scale were reported subsequently in a variety of applications. In the paper industry, the wide use of steam, and cooling and process water gives rise to the usual boiler operation scaling problems. Calcium sulfite scales may also form in sulfite digesters.²³ In addition, increasing concern in the 1950's over the discharge of the dilute waste sulfite liquors, which contain 50% of the original cellulosic material, into rivers and streams led to more recirculating systems, and the indirect heating and evaporation of these spent liquors. Concentration of waste liquor by evaporation prior to further treatment steps had been frustrated by gypsum scaling on evaporator surfaces. The use of calcium sulfate seeding to control this scaling was first reported in Sweden,²⁴ and subsequently developed there as the Escher Wyss gypsum process.²⁵ No details are noted, but the process depends on the addition of a gypsum slurry of "a certain kind" and "in correct quantity and fineness" to the liquor. Whereas cleaning was necessary every five days without seeding, operation for more than 50 days was accomplished with little deterioration of heat transfer performance. This approach would seem to be better than using expensive sequestering agents for cleaning sulfate scales as recommended elsewhere.²⁶ Despite the promise of this approach, it did not appear to have come into general practice following this earlier work.

Recently, French workers²⁷ have reported successful experimental and applied control of scaling by seeding in salt manufacture. In an experimental unit (See Figure 27) scaling was followed by measuring the heat transfer coefficient on a 90/10 Cu Ni tube heated from the inside. Calcium sulfate hemihydrate was used as a seed with less than 100 μ particle size at a concentration 0.1 to 30 g/l. As the length of time the seeds were circulated increased, the mean particle size fell to below 5 μ . Also, after 6-8 hours the hemihydrate was changed into anhydrite -



Source: Reference 27

Figure 39. Apparatus Used to Study Scale Control by Use of Seeds

the stable phase at the temperature of interest (100°C). Reasonable success in prevention of scale was achieved with a seed concentration of 30 g/l and Reynolds number greater than 35,000 (rate of circulation 0.4 - 1.8 m/s which is equivalent to Reynolds number of 16,000 to 65,000). It was shown that the deposition rate of scale depended both on the hydrodynamic velocity and the concentration of seeds. Circulation velocities had to be sufficient to cause turbulence. The optimum seed crystals were anhydrite at a particle size less than 20 μ and concentration of 20-30 g/l.

Since 1966 the method was successfully used to prevent calcium sulfate scales in a NaCl salt factory at Varengeville under the following conditions:

Concentrate composition

NaCl	309	g/liter
CaSO ₄	4.08	g/liter
MgCl ₂	0.7	g/liter
CaCl ₂	0.2	g/liter

Seed composition (anhydrite + Mg(OH) ₂)	20-30 g/liter
Particle size	6-25
Circulation velocity	1.2 m/s
Reynolds number	100,000

The evaporator was a five-effect unit. It was found necessary to prevent boiling from taking place in the tubes. No scale has been formed on the heat transfer surfaces since start up of the plant in 1966.

Refining of Sugar

In the sugar industry, seeding has shown some promise for scale control in evaporators.^{28,29} As the cane juice is evaporated, the calcium sulfate and calcium phosphate rise in concentration and may precipitate. In addition, other calcium salts are present which have inverted solubility curves - acetate, citrate, maleate and oxalate. Sugar evaporator scales are typically composed of silica and calcium sulfate, phosphate and oxalate. An early Norwegian patent described the addition of scale forming substances as seeds.³⁰ This approach was subsequently supported by experimental work and observation of operating plants.^{31,32} However, no systematic application of this technique apparently resulted in this industry either.

Salt Manufacture

In the manufacturing of salt, seeding has been more successful. Evaporation of the brines from which the salt crystallizes first causes precipitation of calcium sulfate which tends to deposit scales on the heat exchanger tubes. In the Alberger and Grainer processes for salt production, the hottest tubes must be drilled out on a twice daily to weekly routine. It has now become regular practice to return a small amount of pan brine containing calcium sulfate crystals to the evaporator to act as preferential nuclei for deposition of the calcium sulfate.³³ Suspensions of 20 grams per liter have been found to be optimum, and have eliminated the scaling problem in vacuum pans. Even when running an unpurified brine, salt evaporators may now be operated for 1-2 years without having to be drilled out,³⁴ and the process has been patented.

The control of scale in boilers has been advocated by the addition of calcium carbonate slurries.³⁶

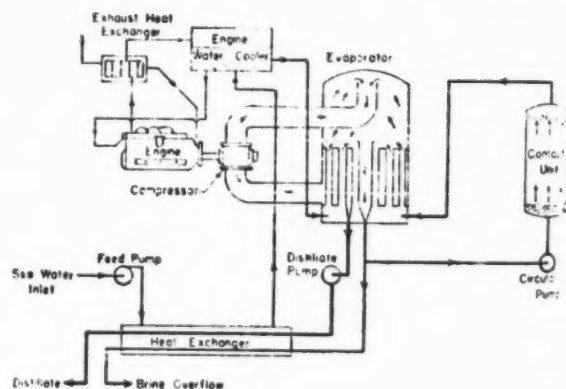
Desalination

A slightly different method of scale control which closely follows the approach of seeding and which showed initial success is that of contact stabilization.³⁷ When studies showed that the supersaturation of CaCO_3 , $\text{Mg}(\text{OH})_2$ and CaSO_4 solutions in seawater was stable over considerable periods, it was suggested that the brine in seawater evaporators should be continually circulated through material which would nucleate the supersaturated solutions and precipitate the salts thereby reducing supersaturation in the heat exchanger. Such a unit is shown in Figure 40.

In a small experimental unit with a potential scale factor* of 1.9 lbs/1000 gal. of distillate, 0.87 lbs./1000 gal. were deposited in the evaporator without contact stabilization, but only 0.09 lbs./1000 gal. with contact stabilization using limestone. In the larger unit illustrated above (60 gallon/hour) contacting with sand reduced the scale from 0.84 lbs. to 0.11 lbs. from water with a potential scale factor of 1.1 - 1.3 lbs./1000 gallons distillate. This method might usefully be applied to a wet scrubber if it is found that the liquid enters the scrubber unnecessarily supersaturated.

Interest intensified in the use of seeding for scale control in the 1960's during the development of seawater evaporators, stimulated by the activities and investments of the U. S. government Department of the Interior Office of Saline Water (OSW). At the Wrightsville Beach OSW demonstra-

*"Potential scale factor" is a useful concept used in the desalination industry to indicate the quantity in lbs. of precipitated salt expected as the brine is concentrated to produce a given quantity of distilled water - usually 1000 gallons.



Source: Reference 34

Figure 40. A Vapor Compression Seawater Distillation Unit
Fitted with a Contact Stabilization Unit

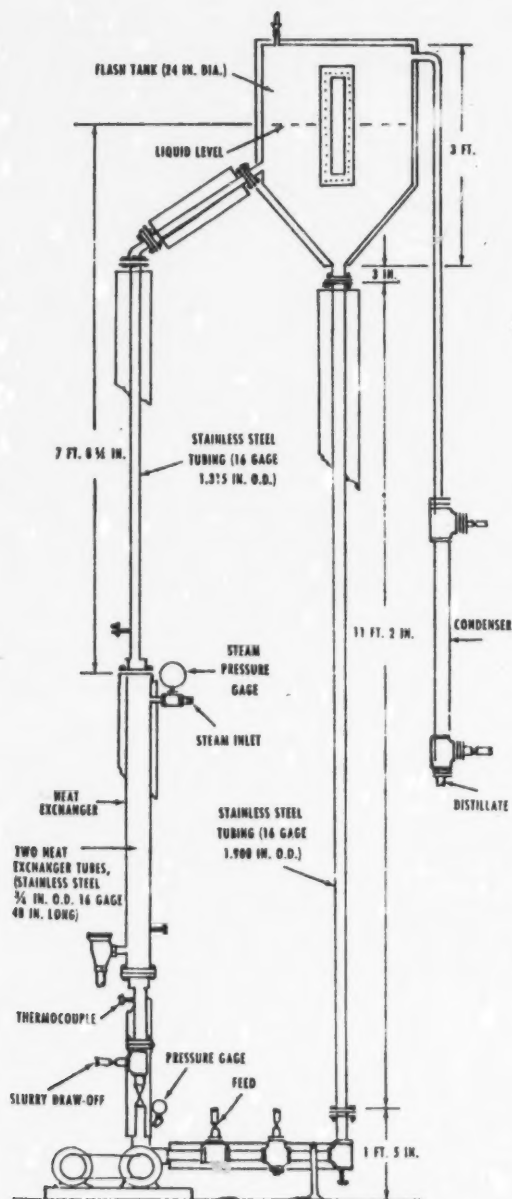
tion plant, a pilot plant long-tube-vertical (LTV) single-effect flash evaporator was used³⁸ in an evaluation of seeding for scale control. CaCO_3 , CaSO_4 and $\text{Mg}(\text{OH})_2$ seed crystals were evaluated under a variety of conditions. Using a "backward feed" method of operating, in which increasing concentrations of brine occur at increasing temperatures, CaCO_3 seed at a concentration of 0.5 - 1% prevented scale formation from clean seawater for week long runs at a feed temperature of 190°F., boiling temperature of 192°F. and overall temperature differences of 8-10°F. CaCO_3 seed could not prevent CaSO_4 scale at higher temperatures (above 200°F.), either alone or in combination with either anhydrous or calcium sulfate dihydrate. This scale was found to be calcium sulfate hemihydrate but this salt could not be used for seeding as it "set up to plaster at every pocket where the liquid could cool slightly." "Forward feed" operation was then initiated in which the calcium sulfate solubility limit is never exceeded. At 250°F., rapidly scaling $\text{Mg}(\text{OH})_2$ was not affected by the presence of solid CaCO_3 seed crystals, but a slurry of solid $\text{Mg}(\text{OH})_2$ (3-5 gram/liter) prevented such a scale for more than a week.

Following this work, seeding was proposed as a method of scale control at both the Roswell and Freeport OSW demonstration plants. The problem at Roswell, a vapor compression plant, was particularly severe³⁹ as the calcium concentration in the Artesian well water feed was more than twice that of seawater (918 ppm vs. 410 ppm) with the sulfate concentration about the same (2,886 ppm vs. 2,710 ppm). An alarming scaling potential of 20 lbs./1000 gallons of distillate or 10 tons per day was expected at the designed brine concentration factor* of 4. Laboratory work indicated that a 1% by weight slurry of calcium sulfate prevented scale during a 176 hour test in a laboratory unit (See Figure 41) at a brine concentration factor of 5 and steam at 6-7 psig; without the solid phase present calcium sulfate deposited on the heat exchanger walls reducing the heat transfer coefficient from about 650 to 225 (BTU/F², °F, hour) in only 38 hours at a brine concentration factor of only 2.8.

It was believed that calcium sulfate slurry of 0.5% by weight would be adequate, but experimental difficulties prevented such an evaluation. Both synthetic water and real water samples gave the same results. Conclusions were confirmed in a two-stage 1600 gallons per minute pilot plant evaporator at Wrightsville Beach, North Carolina.

In other work, a recycle system in a six-stage evaporator using calcium carbonate seeds was operated for 200-300 hours without scaling^{40,41} up to 275°F. Calcium sulfate was ineffective. Settling and entrapment of seed crystals is a continuing problem.⁴² Work in England showed that calcium sulfate hemihydrate was partially effective in preventing sulfate scale, and a comprehensive theory for seed recycle operation was presented.⁴³

*"Brine concentration factor" is the ratio of the volume of the incoming water to the final brine volume after evaporation and at blow down.



Source: Reference 36

Figure 41.A Laboratory Forced Circulation Evaporator Used to Test Calcium Sulfate Seeding as a Method of Scale Control

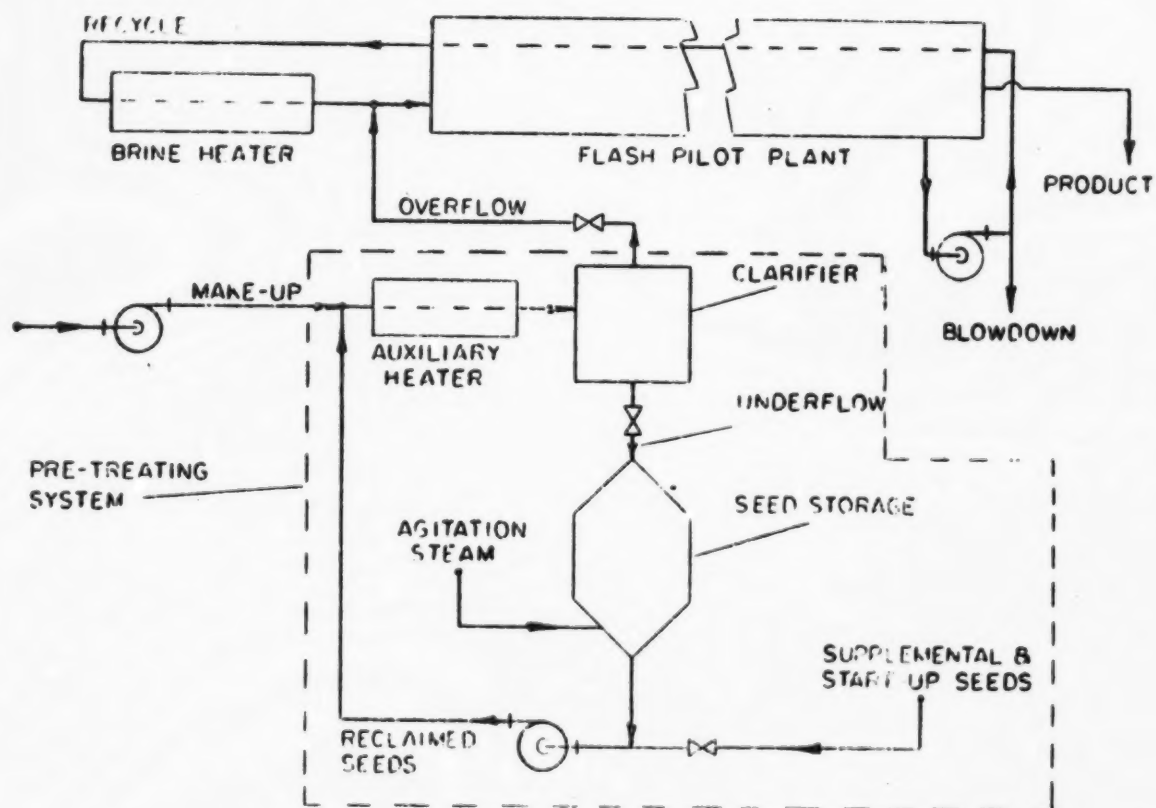
Japanese workers⁴⁴ have found that clay in suspension ("Kuriverter" was its commercial name) acted as a scale prevention agent by nucleation of scale forming precipitates. With 200 mg. per litre in the feed water the amount of deposited magnesium hydroxide scale in a test unit was reduced by one fortieth. Supersaturation of magnesium hydroxide in the liquid was also reduced.

Most experience at OSW plants has been less encouraging. At Point Loma, San Diego, seeds were found to become incorporated into the scale rather than preventing it.⁴⁵ A grinder was subsequently found necessary at Roswell to ensure that the particles remained small and therefore active. At the Freeport, Texas, multistage flash evaporator (MSF) plant, magnesium hydroxide seeding was abandoned when silt build up problems were encountered, seeds grew too large,⁴⁶ and carbonate scales continued unabated.⁴⁷ In general, OSW has found that acid, threshold (q.v.) or water presoftening methods of scale control have been more successful than seeding.

Somewhat more recently, work for OSW by Baldwin, Lima and Hamilton (no longer active in this technology) demonstrated effective scale control in an exploratory test with calcium sulfite seeding in a 16-stage flash distillation pilot plant operated at 275°F. and at a concentration factor of 1.6 far into the scaling range.⁴⁸ No sign of fouling of heat-transfer surfaces occurred. The flow circuit is illustrated in Figure 42.

More optimistic results on the use of seeding in scale control in seawater plants has been reported⁴⁹ by Russian workers, and their interest continues. Work on the use of CaCO_3 and CaSO_4 seeds to prevent scales in the production of table salt from seawater had shown them as early as 1955 that so long as boiling took place away from the heat transfer surfaces, the treatment was successful, even after 10-14 days, compared to the severe scaling normally encountered within 9-11 hours. They showed by electrically heating a stainless steel tube in calcium bicarbonate solution that scaling is intensified at locations where vapor bubbles are formed and in the paths taken by bubbles across the heat transfer surface. In a 4 ton/hour experimental multiple effect plant, scaling was followed by monitoring heat transfer coefficient. Finely-ground natural chalk prevented scaling in the first evaporator at a boiling temperature of 115°C., even though $\text{Mg}(\text{OH})_2$ was the principal precipitate. However, in the subsequent efforts where boiling took place in the heating tubes, scale was deposited. The minimum seed concentration with elevated boiling zones was 5 Kg/m^3 at 90°C., and 15 Kg/m^3 at 115°C. A 90 day run was completed free of scale.

Attempts to control calcium sulfate scale in a three-stage vertical tube evaporator train at brine concentration factors of 4-5 were initially less successful. Scale formed on the tubes and the interesting observation was made that while the scale had a definite anhydrite structure, the slurry adopted an amorphous structure. The reason may be that the temperature cycling caused the crystals to partially convert from one hydrate to another, but never to completion. When the slurry was circulated separately in each unit at a constant temperature, prevention of scaling was achieved for 15 days of operation. The following conditions were used:



Source: Reference 45

Figure 42. Slurry Recycle Process Used in a Pilot Flash Distillation Plant

Stage	Boiling Temp. °C.	Slurry Concentra- tion Kg/m ³	Seed Composition
1	108-112	140-200	CaSO ₄ + CaSO ₄ · 0.5 H ₂ O + CaCO ₃
2	65-70	30-40	CaCO ₃
3	40-45	20-25	CaCO ₃

A vertical tube multiple stage distillation plant with elevated boiling zone was constructed ⁵⁰ at Shevchenko in the USSR to make use of these results: co-current flow was used - the first stage boiling temperature being 90-95°C., the last 40°C. and the brine concentration factor being 4-4.5 (50-60 gram/liter of salt). These temperatures are low enough so that calcium sulfate will not precipitate. The concentration of seed crystals varied from 20-22 Kg/m³ in the first effect to 40-45 Kg/m³ in the fourth effect (ground chalk). Circulation velocities varied from 0.9 to 2.5 m/sec. Later (1965), the temperatures were raised to a range of 110°C. to 50°C. The plant operated from 1963 to 1967 ^{49,50} without deposition of scale. During operation the Mg(OH)₂ content of the seed crystals tended to increase to a limit of about 7.5 wt/% of Mg (Ca at 14.1 wt/% and then stabilize.

Later, a seven stage horizontal flash plant was constructed ⁵¹ to further study this method. Caspian seawater was used which, though less saline than ocean seawater, contains similar amounts of scale forming materials.

Calcium	ppm 400
Magnesium	ppm 778.2
Ruthenium	ppm 207.4
Sulfate	ppm 3059.17

Seed crystals of common ground chalk were used, and heat transfer coefficients were monitored with time. Although scale formation was delayed at temperatures of 125°C. and 115°C., a dense white scale was eventually deposited with the composition

CaO	40.60
MgO	1.07
RuO ₃	20.16
SiO ₂	1.12

that is a calcium carbonate, calcium ruthenate mixture. At 105°C. only small quantities of scale were formed and contained large proportions of corrosion products. At 95°C. no scaling was detected.

Summary

1. Seeding with chalk, $\text{Mg}(\text{OH})_2$ and calcium sulfate has been shown to prevent or reduce scaling from supersaturated solutions under a variety of conditions.
2. Optimum concentrations of seed range from 0.5 to 5% by weight.
3. Several difficulties have been encountered which must be anticipated in any new application of the technique, such as:
 - a. sludging and build up of seed particles in stagnant zones - particularly with calcium sulfate hemihydrate
 - b. if temperature cycled, seeds of calcium sulfate may lose their crystalline form and become less effective
 - c. the presence of calcium sulfite reduces the efficiency of calcium sulfate seeds
 - d. effectiveness is a function of both seed concentration and solution velocity
 - e. grinding may be necessary to keep recirculated seed crystals small and active.

In practically all cases where successful inhibition of scaling has been demonstrated by use of seeding, the system concerned had quite different properties to that of wet scrubbing slurries. Temperatures were frequently higher. No experience is reported for conditions in which calcium sulfite is precipitated. The varied experience reported by different workers for the same scaling system adds to the uncertainty about the effectiveness of seeding in the wet scrubber system. Only by experimentation will its usefulness be evaluated.

Scale Control by Threshold Treatment

Other than water pretreatment to remove scaling agents and pH control, the most common method for scale prevention used in contemporary desalination processes makes use of a poorly understood but fortuitous phenomenon known as threshold treatment. Small quantities of certain polymeric electrolytes inhibit scale growth when present in far less than stoichiometric amounts. These substances are primarily polyphosphates, but other poly-electrolytes have been shown to have the same effect.

Sodium hexametaphosphate (Graham's salt) was first used to treat boiler water. But here it was used as a sequestering agent to solubilize calcium and magnesium salts which might otherwise form scale. As much as 14 parts of phosphate to 1 part of calcium was typically employed. Later it was discovered⁵² that hexametaphosphate prevented deposits of calcium carbonate in ammoniated irrigation water at a level of only 2 ppm, even though the carbonate was present at 200 ppm, and was in fact no more effective at higher concentrations--hence the term "threshold treatment". Since then, this method has been widely used in scale control in cooling water systems, heat exchangers and boiler feed lines, often in proprietary formulations. For example, a mixture of sodium tripolyphosphate, liquid sulfonate and antifoaming agent was promoted⁵³ for seawater evaporators.

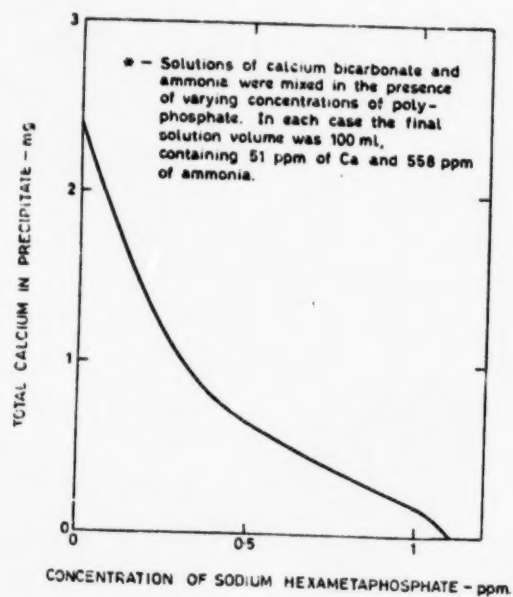
Polyphosphates are degraded in aqueous solution by hydrolysis⁵⁴; the high members trimetaphosphate and tripolyphosphate reverting to orthophosphate. While at room temperature the rate is extremely slow, increasing temperature and falling pH accelerates the decomposition. The times for 5% hydrolysis at 50° C. are as follows:

<u>salt</u>	<u>time to 5% hydrolysis at 50° C.</u>			
	pH	hours		
		<u>4</u>	<u>7</u>	<u>10</u>
pyrophosphate		24	105	2000
triphosphate		9	60	300
long chain		60	900	900

Source: Reference 54.

Calcium Carbonate Deposition

The effect of the addition of polyphosphate on the precipitation of calcium carbonate is shown in Figure 43.



Source: Reference 54

Figure 43. Effect of Sodium Hexameta Phosphate on the Precipitation of Calcium Carbonate

The threshold dose of 1 ppm indicated in Figure 43 has been found to be dependent on the pH (which, of course, affects the bicarbonate concentration in solution) but to be independent of the calcium concentration.⁵⁶ The presence of neutral salts tends to reduce the threshold dose; potassium hydroxide improves the efficiency of the hexameta-phosphate⁵⁵ in suppressing precipitation despite the increased pH.

Effective materials include sodium hexametaphosphate, pyrophosphate,⁵⁵ tripolyphosphate⁵⁶ and linear polymers. As is found in the case of the polyacrylates described later, crystals formed in the presence of polyphosphates⁵⁵ are distorted, but the crystals contain much less of the additive. (Calcium to phosphate ratio about 320-350 to 1) than in the case of the organic polymers (as much as 40% by weight, q.v.).

Although hexametaphosphate addition has been found to greatly increase the negative mobility of the calcium ion as though strong negatively charged complexes were formed,⁵⁴ and the amount of lanthanum or magnesium ions needed to reverse this mobility is then much greater, the dose of polyphosphate in threshold treatment is too low for such sequestering mechanism to be tenable. It has been shown that surfaces treated with hexametaphosphate retain their scale retarding properties when contacted with supersaturated carbonate solutions not containing the phosphate. This evidence combined with the observation of distorted crystals suggests a surface absorption mechanism in which crystal nucleation and growth is inhibited.⁵⁷

Calcium Sulfate Deposition -

Indications that polyphosphate could inhibit calcium sulfate dihydrate deposition at room temperature was shown as early as 1954,⁵⁸ although high doses in greatly supersaturated solutions were needed. Strontium sulfate supersaturation is also stabilized:⁵⁹ a ten-fold increase in polyphosphate concentration reduced the nucleation rate by a factor of about 10⁹.

Magnesium Hydroxide Deposition -

Tripolyphosphate has been found much less effective on magnesium hydroxide scales:⁵⁴ a 2 ppm dose reduced calcium carbonate deposition by 99%, magnesium hydroxide by only 40%. An increased dose was no better.

Other Inorganic Agents -

Many other inorganic materials have been tested⁵⁵ for use in threshold treatment

56 and:	tetraborates	antimonates
	metaborates	arsenates
	orthovanadates	arsenites
	meta vanadates	potassium nitrate
	bismuthates	
	nitrates	metasilicates
	iodates	

but none showed a threshold scale prevention effect.

Use in Seawater Evaporators -

Extensive study has resulted in the successful use of polyphosphates for scale control in seawater evaporators. 'Hagevap' is a proprietary and commonly used polyphosphate formulation which has been particularly successful in the flash evaporators in Kuwait⁵⁶ where it has been used since 1955. The following conditions were found to be satisfactory:

'Hagevap' concentration 4 ppm in feed water,
Water velocity greater than 1.7m/sec., in the condenser tubes,
Water temperature less than 91°C.,
No boiling in tubes and minimum tube surface temperature,
Maximum salinity 70,000 ppm with low iron content.

This success in Kuwait⁶¹ permitted modifications to be made to another plant in Ceuta, Spain to enable it also to run with Hagevap. Successful use of Hagevap at a plant in Las Palmas, Spain was reported.⁶² Sludging using Hagevap has been controlled using Taprogge techniques (circulating rubber balls).

At Ceuta, cost comparisons of various treatment chemicals, mostly based on polyphosphates, were made yielding the following results: ⁶¹

<u>Product Name</u>	<u>Chemical Type</u>	<u>Relative Cost of Water</u>
Hagevap LP	polyphosphate formulation	1.00
Hagevap PD-8	polyphosphate formulation	1.00
Evap. Treatment No. 5	polyphosphate formulation	1.19
Evap. Treatment No. 10	polyphosphate formulation	1.06
Darex 40*	polyelectrolytes	1.05
AC-1	polyelectrolytes	promising

*was not tested at maximum permissible temperature.

The United States Government Office of Saline Water (OSW) has also found polyphosphate treatment to be an effective method for alkaline scale control. One of the most comprehensive early programs which found Hagevap treatment successful was at the Point Loma flash evaporation plant in San Diego.^{45,63} Two thousand five hundred hours of operation was achieved at 200° F. without the need for cleaning. The polyphosphate was used at a level of 4 ppm; the calcium concentration being 400 ppm and the magnesium 1200 ppm. Iron, which is known to interfere with the effectiveness of polyphosphates, was always less than 0.1 ppm. Polyphosphate treatment was also found⁴⁸ to be successful at Freeport, Texas (using a dose of 4-6 ppm) and partially at Guantanamo Bay, Cuba, although sludging was experienced--possibly due to the presence of iron.

Thus, Hagevap polyphosphate treatment is effective and cheaper than polyelectrolytes, but its high temperature instability limits its usefulness in high temperature distillation plants.

In addition, the presence of the polymer makes the crystals much smaller and distorted. The mechanism proposed is that the nucleation sites are masked by absorption of the polymer. Indeed, scales formed contained as much as 40% of the organic material, which indicates that in precipitation conditions such as in scrubber operation considerable attenuation of the polymer would be expected with associated economic penalties.

Dilatometry has also been used to follow the crystal growth of calcium sulfate.⁶⁸ Once again induction periods were shown to be lengthened and growth rates reduced by the addition of polyelectrolytes--0.87 ppm of a copolymer of methylvinyl ether and maleic acid increased the induction period from 15 to 95 minutes, for example. The following generalizations were made as a result of this work:

1. Polymers containing carboxyl groups were most effective, particularly if the groups were neighboring,
2. The higher the concentration the greater the effect.
3. A molecular weight in the region of 1600 was optimum.
4. With carboxyl groups the effectiveness increased with pH, roughly following the degree of association of the carboxyl groups.

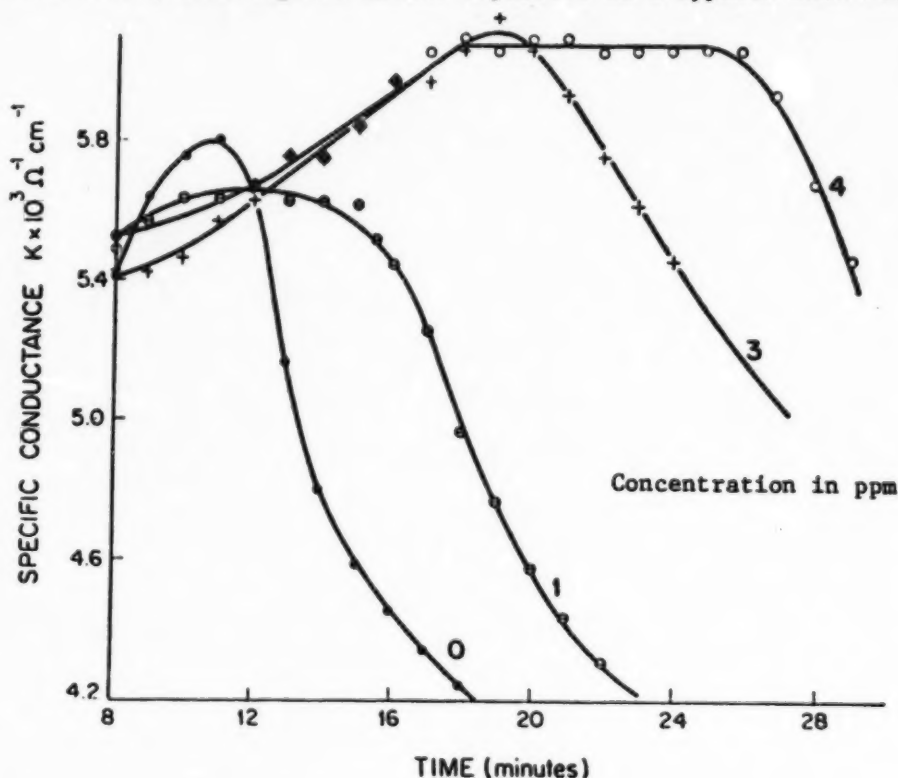
Reports that acrylic based polymers yielded self-cleaning scales^{65, 69} are found^{45, 70} to be probably dependent on the synergistic presence of small amounts (~0.2 ppm) of aluminum, magnesium or zinc. In addition, difficulties in obtaining reproducible scales in experimental work was found to be due to the occasional presence of a derivative of polyethylene oxide, leached from the polythene storage bag. The authors noted that it appeared to be an effective scale prevention agent. Storage in high density polythene avoided this difficulty.

Scales formed in the presence of both polyelectrolytes and the metal ions above were found to strip easily from the copper surfaces of a laboratory spray evaporator on exposure to air. Once again, the lower molecular weight materials in the range 1000-1600 were most effective. This work indicates how sensitive scale formation is to precise operating conditions particularly with respect to trace impurities in the system. This could explain different experiences in scrubber operation and in experimental studies in scales.

In Kuwait also, following the success of Hagevap treatments, attempts were made⁷¹ to find higher temperature polymers to permit operation at 200° F. and above. Both "beaker" and plant tests were carried out to study suppression of alkaline scale. The following results were obtained:

Studies of Polyorganic Compounds:-

The success of polyphosphate treatment at low temperatures led to considerable efforts to find other materials with the same activity, particularly with effects on calcium sulfate scales and with improved stability at high temperatures. A range of acrylic acid homopolymers and copolymers was synthesized and tested for alkaline scale suppression in a pilot plant evaporator at around 3 ppm. A screening test was developed in which saturated carbonate, hydroxide and sulfate solutions were boiled down in beakers in the presence of various additives and the quantity of scale produced measured. Promising results were obtained with polymers below a molecular weight of 30,000. In particular one polymer composed of acrylic acid, ethyl acrylate, and isopropyl acrylate in the ratio by weight of 61:10:29 with a molecular weight of 19,000 showed particular promise for inhibiting calcium sulfate scale, reducing the amount deposited in a typical test from 42 mg



Source: Reference 66

Figure 44 Effect of Polymer Concentration on the Inhibition of Gypsum Crystallization

to 2.4 mg at a concentration of only 7 ppm. In the pilot plant tests, it showed excellent scale prevention in respect to $\text{Mg}(\text{OH})_2$. Sulfate scale deposition showed a minimum at an acrylic acid composition of about 60% in the range of copolymer formulations evaluated.

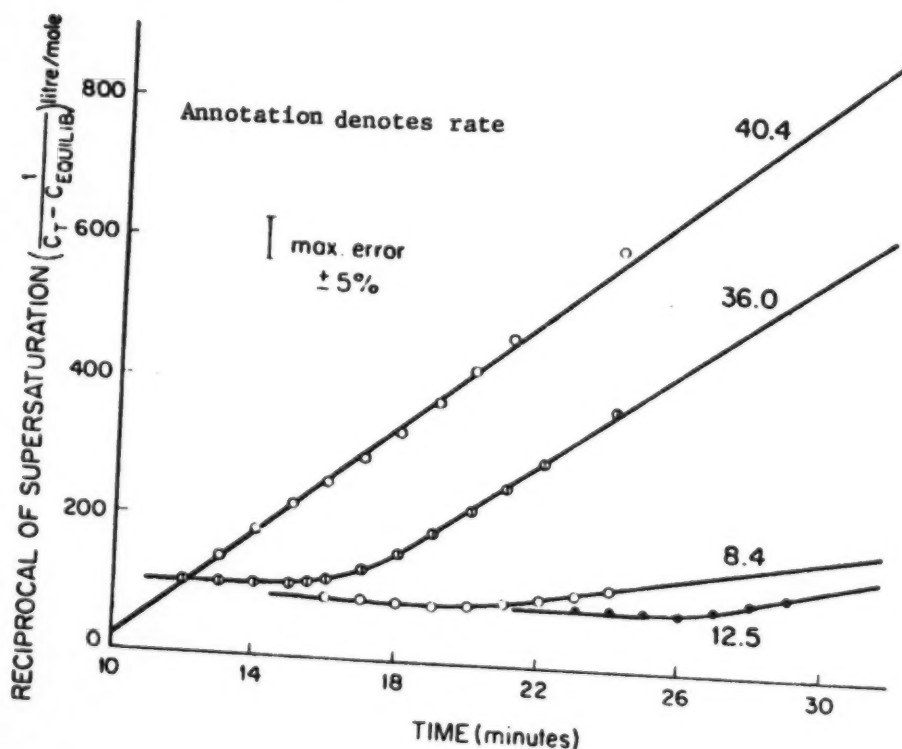
Using a polymer of this type containing 66% acrylic acid, it was shown further by using conductance measurements to follow ionic concentration, that

the mechanism of scale suppression was an interference with crystallization kinetics which results in modified crystal habit. During the boiling down of calcium sulfate solutions in the beaker tests, specific conductance increased as the concentration rose, but then fell rapidly as the scaling rate exceeded the rate of concentration of the solution. Figure 44 shows the effect of concentration at 100°C. Four ppm was sufficient to extend the period for initiation of significant precipitation from 10 minutes to 25 minutes.

Interestingly the second-order dependence of scaling rate with supersaturation⁶⁷

$$(C_T - C_{\text{Equilib}}) = K \frac{1}{T}$$

(where C_T is the concentration at time T , C_{equilib} is the thermodynamic equilibrium solubility and K is constant) C_{equilib} is maintained but the presence of the polymer introduces an induction period, and at 3 and 4 ppm radically decreases the rate of crystallization. This effect is dramatically illustrated in Figure 45.



Source: Reference 66

Figure 45. Reciprocal of Supersaturation as a Function of Time for Gypsum Solutions Crystallizing at 100°C in the Presence of Polymer.

Top line: 0 ppm treatment
2nd line: 1 ppm treatment

3rd line: 3 ppm treatment
Bottom line: 4 ppm treatment

<u>Compound</u>	<u>Composition</u>	<u>Test</u>	<u>Temperature</u>	<u>Dosage ppm</u>	<u>Result</u>
Darex 40 (W. R. Grace)	Sodium polyethacrylate (25% solids)	Plant	200° F	3-9	Initial cleaning action.
		Beaker	212° F	0-25	Maximum performance at 5 ppm but Mg(OH) not controlled.
Calnox 214 (Milchem)	Copolymer of acrylic acid (33% solids)	Plant	200° and 225° F	1-18	Worked well at the low temperature.
		Beaker		1-25	Optimum dose at 2 ppm.
Calnox 214	Plus sulfuric acid	Plant	200° F	0.75-1.2	Functioned when greater than 1 ppm.
Vaptreat H (Houseman and Thompson)	Includes polyacrylic acid (40% solids)	Beaker	212° F	0-25	Optimum dose at 4-5 ppm.

Thus all the materials behaved well in beaker tests, and in plants at 200° F. where tested. The "threshold-like" dependence of scale prevention on dose is typified in Figure 46 for beaker tests on Darex 40. All the materials tested showed a similar strong reduction in scale deposition as a function of concentration reaching a maximum effectiveness at 4-5 ppm.

Another laboratory study⁷² compared seventeen polymers for the capability in preventing the precipitation of alkaline scales and calcium sulfate from saline and water. At a dose of 20 ppm, the most effective were the anionic low molecular weight materials based on acrylic acid and its copolymers. Even in sodium chloride, the polymers were able to hold more calcium sulfate in solution. For example, with polyacrylic acid (Molecular weight = 5,000) at 22 ppm, the following precipitation points for calcium sulfate were obtained.

	<u>ppm</u>	
	<u>no additive</u>	<u>with additive</u>
water	1,800	4,800
3% NaCl	6,300	11,900

A sharp maximum of effectiveness was found at a pH of 10.3.

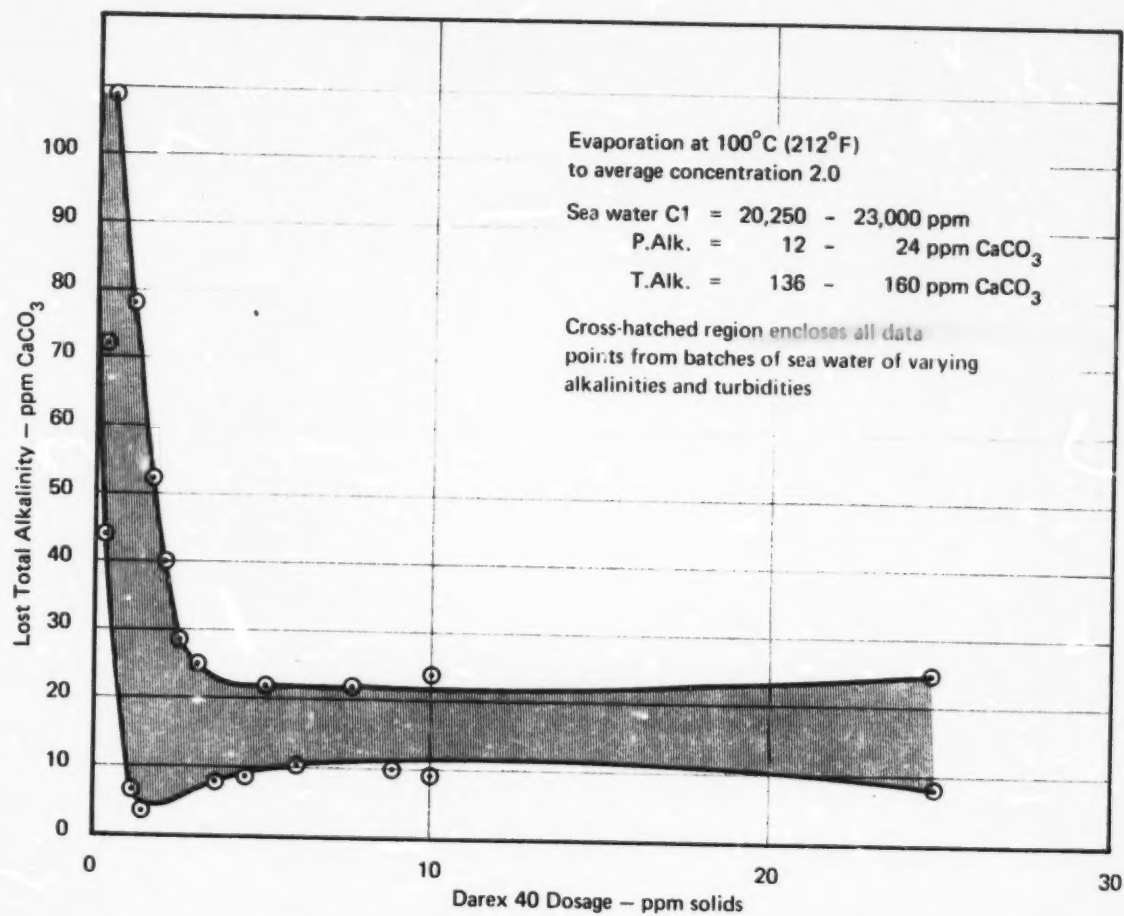


FIGURE 46. ANTISCALING ACTION AS A FUNCTION OF CONCENTRATION OF A POLYETHACRYLATE (DAREX 40)

Summary:

1. Polyphosphates have shown remarkable ability to control alkaline scale at concentrations of 2-5 ppm up to temperatures of 190°F., although less effective for $\text{Mg}(\text{OH})_2$ than for CaCO_3 .
2. Ample evidence exists to show that they will control calcium sulfate scale, but this is of little significance in seawater distillation technology since such scales only occur at temperatures above the stability limit of the polyphosphates. This could of course be useful in scrubber operation.
3. The mechanism of action is thought to be interference with crystal nucleation and growth by absorption at active sites. Nucleation times are greatly extended and rate of growth may be reduced.
4. By synergism with small concentrations of certain metal ions, self-cleaning (loosely adherent and brittle) scales may be formed.
5. Other polymeric anionic materials, particularly the low molecular weight acrylic homopolymers and copolymers show similar activity, and better temperature resistance. The crystal deposits have a large organic content, however, and considerable attrition of material must be anticipated.
6. Their use in other applications, such as wet scrubbing, may involve several difficulties. Traces of other materials may effect the activity. They are chemically unstable particularly at lower pH. Whether they can inhibit precipitation of one species (e.g., calcium sulfate) while precipitation of another (e.g., calcium sulfite) is occurring is doubtful. In systems where large quantities of material are precipitating, attrition of the additive can be expected.
7. Doubts about the mechanism of inhibition and the differences between wet scrubbing slurries and other systems where their effectiveness has been demonstrated points up the necessity of an experimental evaluation of their usefulness in the scrubber system.

APPENDIX I

METHOD OF CALCULATING IONIC EQUILIBRIA

Our method of calculation is to set up the mass law equilibrium equations for all ionic, solid, and gaseous species. Equilibrium constants are calculated for the temperature under consideration using literature data as summarized in the Radian report. Preliminary initial values of the activity coefficients are assumed as follows:

<u>ionic charge</u>	<u>activity coefficient</u>
zero	1.0
one	0.8
two	0.4

The electrical neutrality equation, which equates concentrations of positive and negative species, is then solved to give an approximate value of the calcium activity. The activities and concentrations of all other species are then computed, and fresh values of the activity coefficients are calculated from the ionic strength by using the modified Debye-Hückel expression. This process is repeated until the calculation converges.

The electrical neutrality equations solved for each of the five systems in Table III are quadratics of the form:

$$Aa_{ca}^2 + Ba_{ca} + C = 0$$

where a_{ca} is the activity of calcium in solution. Values of the expressions A, B, and C for each of the four systems are shown in Figure 1A. The various symbols used in Figure 1A are explained in Table 1A.

The program logic and card decks may be obtained from Arthur D. Little, Inc.

In the form: $Ax^2 + B_x + C = 0$ where x is calcium ion activity.

Case	A	-B	-C
1.	$\frac{1}{F_{13}} + \frac{K_{11}}{2A_{11}F_{10}K_{10}}$	$\frac{K_{11}}{2A_{11}F_{12}} - \frac{A_{11}}{2F_{11}}$	$\frac{K_1}{F_1} + \frac{A_{11}K_1}{2K_3F_3}$
2.	$\frac{1}{F_{13}} + \frac{K_{11}}{2A_{11}F_{10}K_{10}}$	$\frac{K_{11}}{2A_{11}F_{12}} - \frac{K_2A_{11}}{2K_4K_9F_9} - \frac{A_{11}}{2F_{11}}$	$\frac{K_1}{F_1} + \frac{K_2}{F_2} + \frac{A_{11}K_1}{2K_3F_3} + \frac{A_{11}K_2}{2K_4F_4}$
3.	$\frac{1}{F_{13}} + \frac{K_{11}}{2A_{11}F_{10}K_{10}}$	$\frac{K_{11}}{2A_{11}F_{12}} - \frac{A_{11}}{2F_{11}} - \frac{A_{11}K_2}{2K_4K_9F_9} + S + \frac{A_{11}SF_{14}}{2K_{15}F_{15}}$	$\frac{K_1}{F_1} + \frac{K_2}{F_2} + \frac{A_{11}K_1}{2K_3F_3} + \frac{A_{11}K_2}{2K_4F_4}$
4.	$\frac{1}{F_{13}} + \frac{K_{11}}{2A_{11}F_{10}K_{10}}$	$\frac{K_{11}}{2A_{11}F_{12}} - \frac{A_{11}}{2F_{11}} - \frac{A_{11}K_2}{2K_4K_9F_9}$	$\frac{K_1}{F_1} + \frac{K_2}{F_2} + \frac{A_{11}K_1}{2K_3F_3} + \frac{K_{14}}{F_{14}} - \frac{A_{11}K_{14}}{2K_{15}F_{15}} + \frac{A_2K_{11}}{2K_4F_4}$

Figure 1A: Quadratic Equations Solved in Equilibrium Calculations.

Table IA. List of Symbols

Equilibrium Constants*		Activity Coefficients		Other Symbols
K ₁	CaSO ₃ · 1/2 H ₂ O(s)	F ₁	SO ₃ ⁻	A ₁₁ activity H ⁺
K ₂	CaSO ₃ (s)	F ₂	CO ₃ ⁻	A ₁₃ activity Ca ⁺⁺
K ₃	HSO ₃ ⁻	F ₃	HSO ₃ ⁻	S dissolved SO ₄ ⁻ concentration
K ₄	HCO ₃ ⁻	F ₄	HCO ₃ ⁻	
K ₅	H ₂ SO ₃	F ₅	H ₂ SO ₃	
K ₆	H ₂ CO ₃	F ₆	H ₂ CO ₃	
K ₇	CaSO ₃ [°]	F ₇	CaSO ₃ [°]	
K ₈	CaCO ₃ [°]	F ₈	CaCO ₃ [°]	
K ₉	CaHCO ₃ ⁺	F ₉	CaHCO ₃ ⁺	
K ₁₀	CaOH ⁺	F ₁₀	CaOH ⁺	
K ₁₁	H ₂ O	F ₁₁	H ⁺	
K ₁₂	SO ₂ (g) + H ₂ O(l) ⇌ H ₂ SO ₃ (soln)	F ₁₂	OH ⁻	
F ₁₃	CO ₂ (g) + H ₂ O(l) ⇌ H ₂ CO ₃ (soln)	F ₁₃	Ca ⁺⁺	
K ₁₄	CaSO ₄ · 2 H ₂ O (s)	F ₁₄	SO ₄ ⁻	
K ₁₅	HSO ₄ ⁻	F ₁₅	HSO ₄ ⁻	

*Solubility products of solid species; dissociation constants of neutral or ionic species

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